NEW SUPERCONDUCTORS

First Semi-Annual Technical Report

August 1, 1970 - January 31, 1971

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CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

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TABLE OF CONTENTS

I. INTRODUCTION

The objective of this program is to study the theoretical and synthetic problems of producing higher temperature superconducting materials. The program consists of four principal sections: a theory section concerned with the development of accurate methods for determining the polarizability of large organic molecules, the extension of existing band theory methods to linear systems and the development of means of using these properties for the calculation of the transition temperature of any superconducting phases; a synthesis section involved in the synthesis of transition metal linear organo-metallic systems of crystalline or covalently bound structures and with special ligand systems for control of the electronic environment of the metal atoms; an x-ray section for determining the structure of crystalline samples; and an experimental section for determining the material parameters of the prepared materials as functions of temperature and pressure.

The initial phase of the program has been directed to each of the theoretical problems mentioned above and to developing synthetic methods for preparing various classes of linear conducting materials. Attention has been directed to the problem of obtaining good single crystal specimens of simple linear organo-metallic system to gain an understanding of the basic electronic properties of such conductive chains. Likewise, attention has been turned to the problem of obtaining reliable values for the conductivity through the use of four probe techniques and kid-glove methods for mounting the miniature fragile specimens.

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II. THEORETICAL PROGRAM

The theoretical program is involved in three principle problems.

A. Exciton Theory

The first is directed to obtaining accurate values for the effective interaction between electrons in the vicinity of a highly polarizable molecule. Methods had been developed earlier for determining the low lying $\pi \rightarrow \pi^*$ excitations in large organic molecules to an accuracy of about 5%. (H. Gutfreund and W. A. Little, J. Chem. Phys. 50, 4468 (1969)) This has been expanded upon to yield the dynamic effective interaction in the neighborhood of a single molecule. After examining a series of possible molecules it was found that the symmetric cyanines and carbocyanines are among the most polarizable. Attention has been concentrated on these. It was found possible to calculate the excited states and oscillator strengths of the principle low-lying allowed states using our earlier methods. This became possible when it was recognized that excellent agreement with experiment could be obtained by assuming that the overlap integral between carbon atoms in the conjugated chain linking the two quinoline nuclei have a smaller value than the ring carbons. This is plausible in view of the strained nature of this chain found in molecular models. The width of the electronic levels play an important role in the frequency dependent part of the electronic interaction. This is determined by coupling to the vibrational modes of the molecule. Rather than attempt to calculate this we have been content to use the empirically observed widths in our work. With these assumptions we find the experimental and theoretical results in good agreement as shown in Fig. 1.

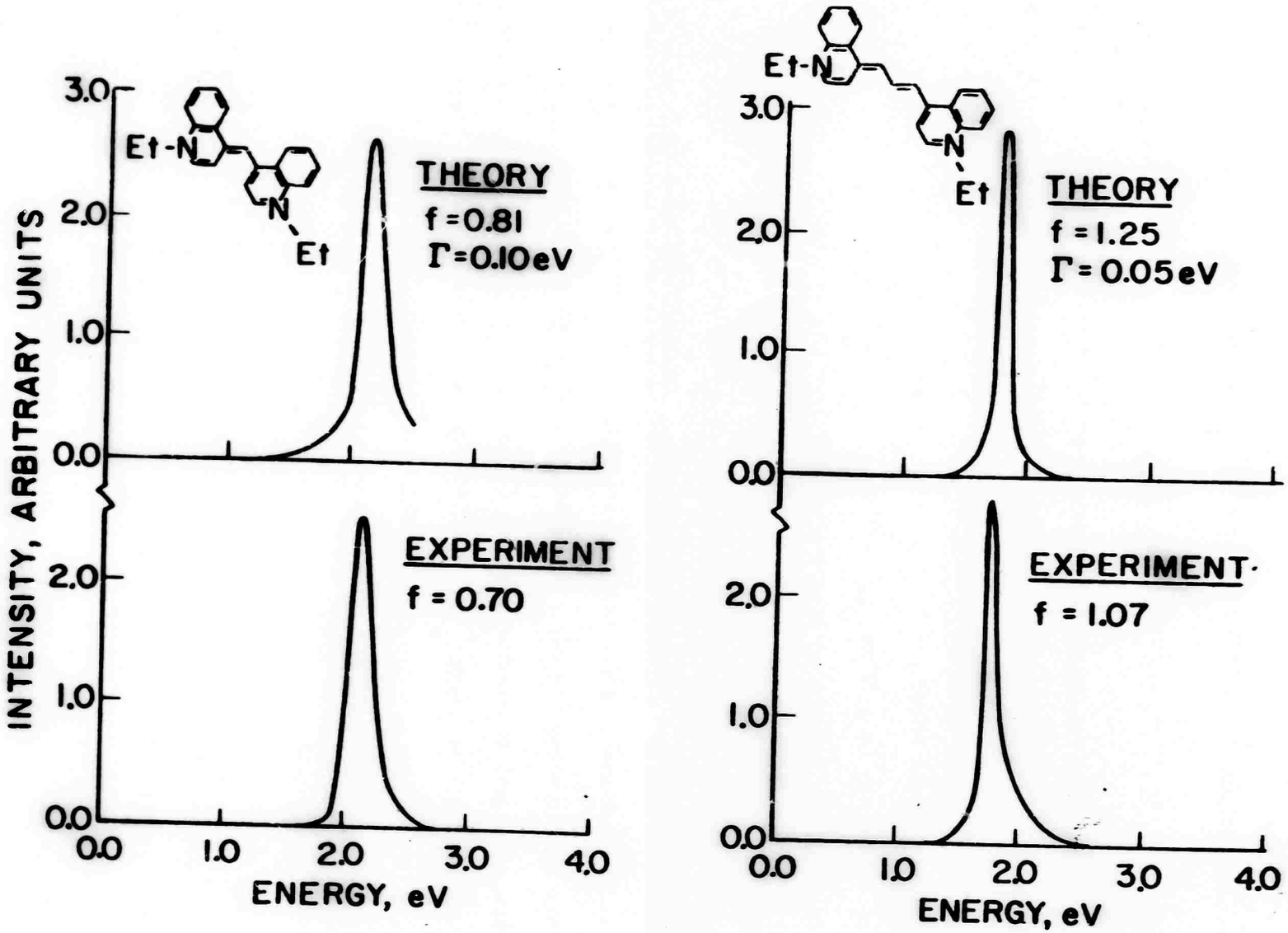
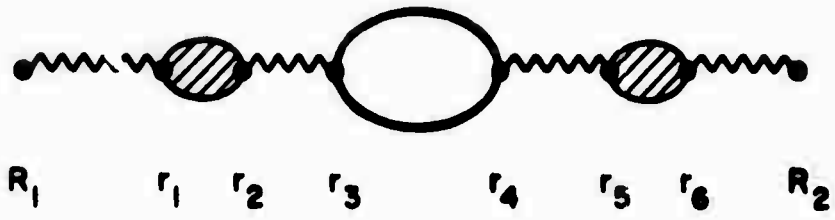


Fig. 1 Theoretical and experimental spectra of the absorption intensity of a 4,4'-cyanine and a 4,4'-carbocyanine dye.

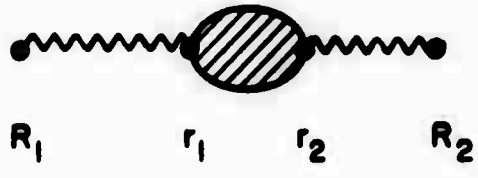
The calculations which yield these results can then be used to calculate the dynamic effective interaction. Provided the bare interaction is not too strong the effective interaction can be represented by the sum of the two diagrams shown in Fig. 2. The first represents the interaction between a charged particle outside the molecule at R_1 interacting with a low lying excited state at r_3 via an interaction which is partially screened by the higher excited states represented by the shaded bubble $r_1 r_2$. This results in an induced charge in the molecule which produces a field at another external point R_2 which is likewise screened by the higher excited states (the second shaded bubble). This represents to first order the excitonic interaction. Fig. 2(b) shows the Coulomb repulsion partially screened by the higher excited states.

Use of these two classes of diagrams yields the time dependent electron-electron interaction. We have considered the case of a molecule situated as shown in Fig. 3 and the net interaction between charges at r_1 and r_2 which lie outside the molecule. A typical result is shown in Fig. 4 for the carbocyanine molecule shown in Fig. 5. In Fig. 5 the relative strength of the attractive component of the effective interaction is shown for each of several points near the molecule. It should be noted that it is not strongly peaked near the nitrogen site but almost equally strong over the whole end of the molecule.

The computed curves for the net interaction are only valid if the strength of the bare interaction is small enough to limit the problem to the set of diagrams discussed above. Outside this limitation the diagrammatic representation of the problem is extremely complicated. However, a useful upper limit on the attractive component from any single dye can readily be found because the molecule behaves essentially as a two level system in the



(a)



(b)

Fig. 2 (a) Diagrammatical representation of the screened interaction (shaded bubble) of an external charge at R_1 with the low-lying excitations of a molecule (open bubble) and the resultant screened response at another external point, R_2. The high energy excitations alone contribute the screening of the shaded bubble.

(b) Diagrammatical representation of the Coulomb interaction between two points R_1 and R_2 lying outside a molecule and the screening (shaded bubble) of this interaction as a result of the high energy excitations of the molecule.

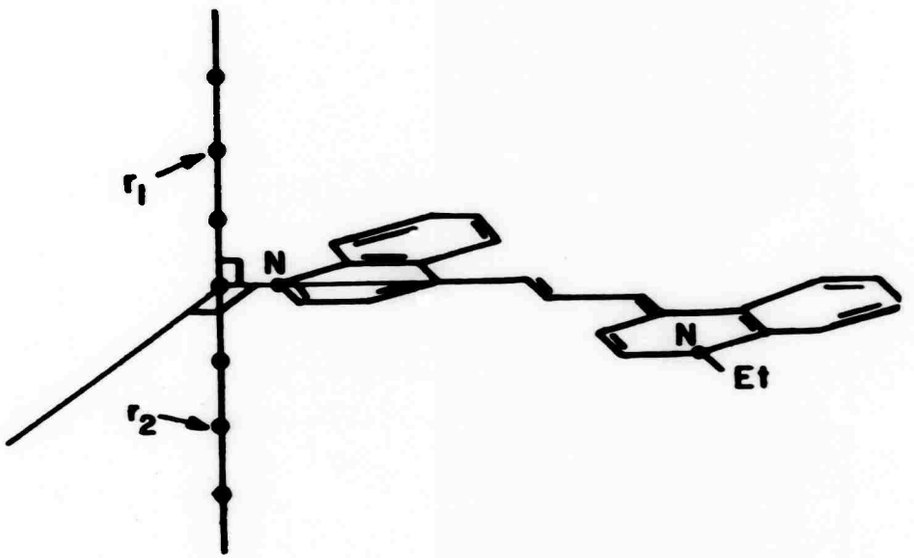


Fig. 3 Orientation of the dye-molecule relative to the points r_1 and r_2 used in the computation of the effective interaction.

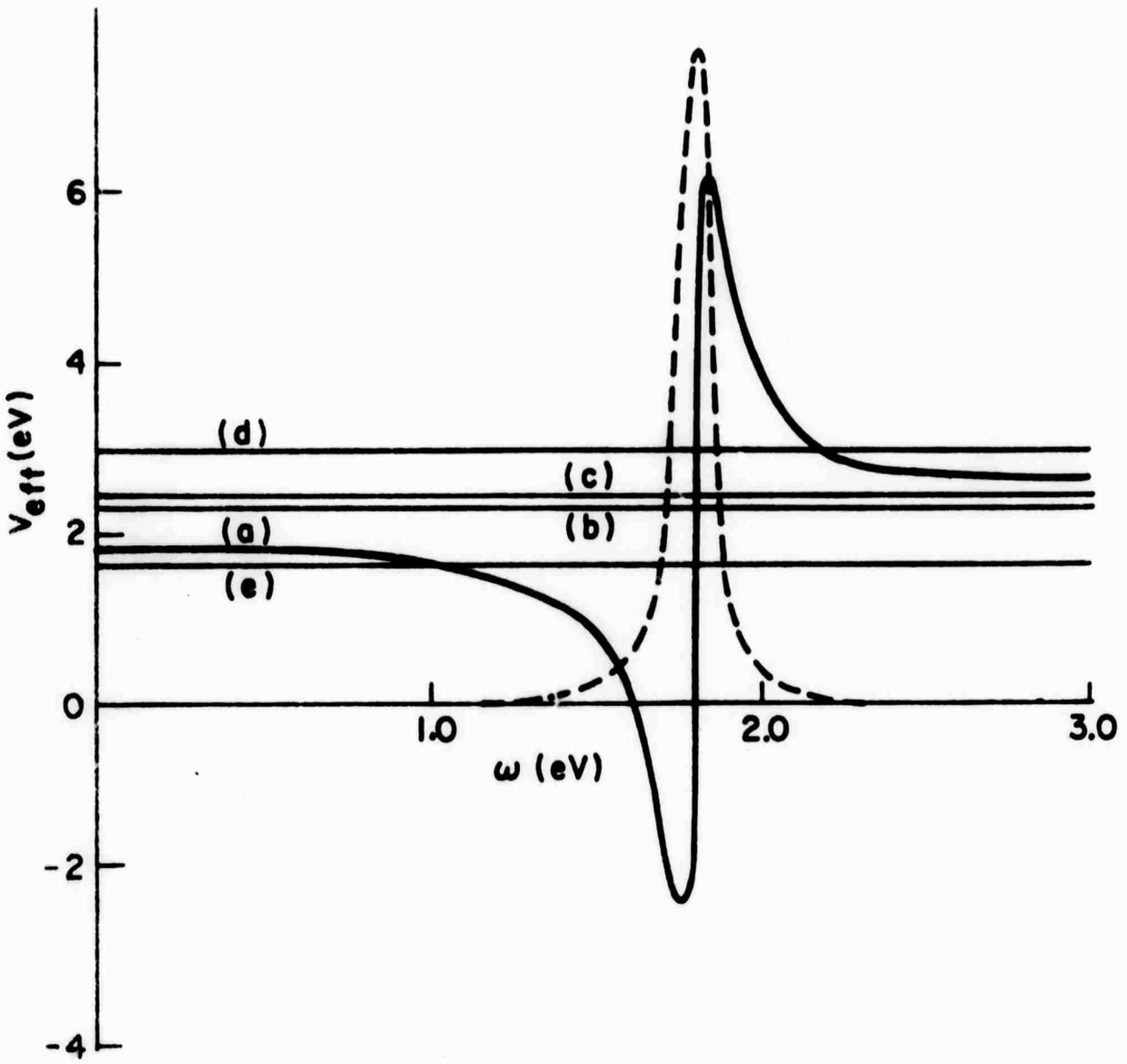


Fig. 4 Effective interaction in the vicinity of the 4,4'-carbocyanine dye, where r_1 and r_2 are 3Å above and below the plane of the dye respectively. Curve (a) is real part of total effective interaction; (b) Coulomb repulsion screened only by higher configuration; (c) unscreened Coulomb repulsion; (d) and (e) limits set by Eqn. (11); dashed curve imaginary part of total effective interaction.

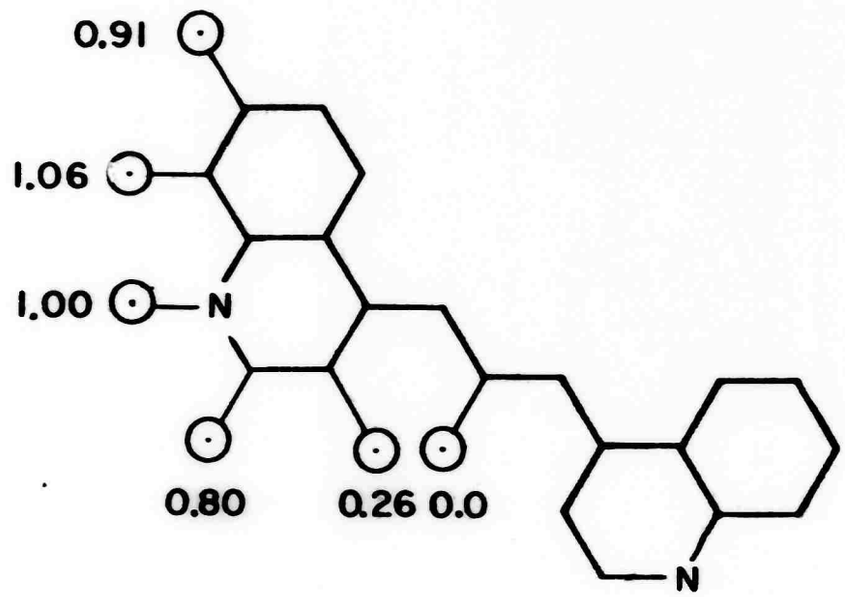


Fig. 5 Relative strength of the contribution from the low lying excitations to the effective interaction for $r_1 r_2$ passing through the given points near the carbocyanine.

frequency range of interest. Elementary quantum mechanics allows one to calculate the maximum field which the molecule can produce when left in a mixture of these two states. The lines d and e of Fig. 4 represent these limits. This provides a useful rule-of-thumb that about three or four dye molecules are required for each useful conduction electron in the conductive spine if a net attractive interaction is to be obtained.

The above results and details of the calculations have been submitted to the Physical Review for publication. We are now working on the problem of finding the effective interaction near a periodic array of such molecules.

B. Band Theory

The second part of the theoretical program is concerned with calculations of the band structure of linear complexes, particularly those of the structure being prepared under the synthesis program. In these compounds the square planar complex of a transition element such as Pt or Ni form a stacked array with a metal-metal bond between the metals in the chain. A significant overlap occurs between the orbitals of the metal in each layer but the overlap between orbitals of the other atoms of the complex is small. The conductivity is known to be highly anisotropic and the overlap between atoms on adjacent chains should thus be extremely small. Conventional methods of calculating the band theory with such a large anisotropy would be expected to give very poor results. Consequently we have had to devise an appropriate method which would be able to handle the one-dimensional nature of this problem in a natural way. These considerations led us to studies of the "Multiple-scattering" model proposed and discussed by K. H. Johnson. (K. Johnson, J. Chem. Phys. 45, 3085 (1966); and K. H. Johnson and F. C. Smith, Phys. Rev. Letters 24, 139 (1970)) This method can handle large molecules or unit cell

structures repeated in any one of one, two or three dimensions. Initial studies indicated that this looked like an attractive method to use being faster than ab initio methods yet of sufficient versatility and accuracy to provide useful guidance in the overall program.

The method is being developed into a computer program by Mr. A. Abarbanel who has been in consultation with Frank Herman's group at IBM in San Jose and with Keith Johnson at MIT. In its simplest form the method may be applied to a small molecule. This is done by drawing a sphere round each atom of the molecule within which the potential is considered to be spherically symmetric. The entire molecule is contained within another larger sphere. Between the atomic spheres and within the large spheres the potential is considered uniform. This is the usual muffin-tin approximation. Outside the large sphere the potential is considered to be zero. Within the atomic spheres the wave function is described by the spherical harmonics and a radial function, and in the uniform potential region of the muffin tin is described by a free Green's function. The boundary conditions which arise at the surface of each sphere give rise to a set of compatibility equations. The values of the coefficients in these equations depends upon the trial energy E of the state. The eigen values for the atomic and molecular orbitals are found from the value of E which satisfies the compatibility equations and the eigen values from the coefficients.

The method handles structures having a repeating unit cell by replacing the single coefficients in the compatibility equations by sums of terms containing the contributions from the other unit cells each shifted in phase with respect to the first shell by a factor $e^{ik\cdot r}$.

Thus far the method is being tested on simple diatomic and triatomic molecules and later will be extended to the linear system. No new results have been

obtained as yet.

C. Energy Gap Calculations

The problem of calculating the superconducting energy gap or transition temperature in a linear system is being studied formally to see if any special simplifications or approximations used in the three dimensional system can be used here. In particular the problems of retardation and the effects of renormalization are being looked at. It is planned to use the results of sections A and B for these calculations once these become available. In the meantime model calculations are planned using a simple form for the effective interaction and a simple metallic or semiconducting band structure.

III. SYNTHETIC PROGRAM

Summary

The synthetic portion of this research project has as a primary goal the preparation of linear conducting materials. To date, all of our efforts have been concentrated on the synthesis of linear polymers with backbones comprised entirely of covalently bonded metal atoms. Both long and short range approaches to the preparation of unidimensional intermetallic polymers have been carried out in parallel.

As a first generation class of such intermetallic polymers, we have chosen to prepare crystalline materials of the type first described by Krogmann. The so-called Krogmann complexes are non-stoichiometric substances existing as chains of equivalent covalently bonded heavy metal atoms (such as platinum and iridium) coincident with the principal axis of the crystal. There are two types--one consisting of anionic metal chains encompassed by ligands such as oxalate or cyanide, and the other neutral with surrounding ligands which balance the overall charge. Each chain of the first type is surrounded by alkali or alkaline earth cations and water molecules. These materials were selected because their preparation is simple and they can be used to initiate our experimental electron transport studies on unidimensional conductors. Furthermore, the possibility exists to introduce cationic dyes into these substances in place of the alkali or alkaline earth cations. Dr. Lin has carried out these studies which are outlined in detail further on.

A larger range aspect of our program has been the attempted syntheses of oligomeric chains of group IVA (Si, Ge, Sn) atoms having precise lengths. After preliminary work on silicon chains, this element was discarded because of the difficulties in bonding transition metals (to serve as electron donor) to silicon. Germanium chains were then examined by Dr. Cooke and Mr. Stark who prepared a series of germanium hexamers and an unsymmetrically substrated digermane for studies of Ge-Ge coupling reactions and transition metal-germanium coupling reactions. Dr. Nelson investigated reactions as models for the coupling of tin atoms on a solid state polymer support in the manner of the Merrifield peptide synthesis. Severe experimental difficulties were encountered in the tin-tin coupling schemes with the result that this portion has been deferred so that sufficient manpower can be focused on the more promising approaches concerned with the synthesis of a growing monomer. Nelson was able to prepare some ill-characterized amorphous, pyrophoric substances which appear to be three dimensional polymers comprised of tin-iron networks. These results are summarized under Cooke, Stark, and Nelson.

The most promising long range approach to the synthesis of linear intermetallic polymers involves the preparation of a monomer having metal atoms held in a rigid linear chain and suitably substrated to self-polymerize. Compounds having the requisite linear array of Sn-Co-Sn have been prepared by Mr. Murphy. His preliminary

results are outlined further on. This approach to intermetallic polymer synthesis is the most promising and is being given priority (see for example the second year proposal).

INVESTIGATIONS OF THE KROGMANN SALTS

Doris Lin

It has been suggested at the Hawaii Symposium[1] to alter the nature of the conducting spine of Little's filamentary superconductor model from a conjugated carbon system to one of columnar "stacked" metal atoms. Ideal systems of this type would be a variety of square-planar d^8 metal complexes, particularly those of Pt, which form structures containing linear chains of heavy metal atoms.[2] X-ray data indicate there is no real bond between the metals, as the metal-metal distances are usually 0.3 to 0.4 Å longer than the expected covalent distances. However, several recent papers[3-7] have shown that some of these square-planar complexes possess anisotropic semi-conducting properties along the metal axis of 10^{-5} to 10^{-10} ohm^{-1} cm^{-1} at room temperature, indicating the existence of direct metal-metal interaction. Moreover, the bonding in some of these linear chains can be strengthened by partial oxidation to give nonstoichiometric compounds which retain the "stacked" structures with the bond lengths reduced by about 0.3 Å. The conductivity in these so-called "Krogmann salts" is as high as 10^{-2} ohm^{-1} cm^{-1}.[8] It seems obvious that these "Krogmann salts" would be ideal model systems for our search for higher temperature superconductors, and would provide some weight in the design and synthesis of linear high molecular weight polymers with actual bonds between metals.

Thus, our main objective in this research project is to attempt to synthesize a variety of "Krogmann salts", with subsequent growth of suitable single crystals for electrical measurements. At present, the

known "Krogmann salts" contain only oxalate and cyanide as ligands of platinum, and with metals of groups I and II as counter ions. We have concentrated most of our time on the oxalato complexes, but will soon be looking at the cyanide complexes and also search for other possible ligands. So far we have been successful in making the partially oxidized K, Na, Ca, and Mg compounds; but we only succeeded in growing small single crystals of the K and Mg salts. We have done some preliminary crystallographic studies on the K and Mg salts, although no formal conclusion has been reached on the size of the unit cell yet.

Experimental Section

The formation of the oxalato complexes was done by: (1) neutralization of the concentrated blue solutions of the acids, $H_2Pt(C_2O_4)_2$, with the corresponding bases or carbonates. (2) Decomposition of the yellow $K_2Pt(C_2O_4)_2$ with the corresponding nitrates, chlorides or perchlorates. (3) Addition of an equivalent amount of the corresponding halides to the yellow $Ag_2Pt(C_2O_4)_2$.

Potassium dioxalatoplatinate(II) $K_2Pt(C_2O_4)_2 \cdot 2H_2O$. This yellow salt was prepared according to Vèzes.[9] Two grams K_2PtCl_6 (orange-yellow powder) was suspended in a solution of 0.8g $K_2C_2O_4 \cdot H_2O$ in 10 ml H_2O. The mixture was stirred at 70° until all the CO_2 has evolved and a brownish-red solution resulted (about 6-7 hours). An additional 2.0g $K_2C_2O_4 \cdot H_2O$ was added and stirred for about 5 hours at 70°C until yellow precipitate formed. The solution was cooled to 0° and was filtered. Yield ~75%. The crude product was recrystallized from hot water and formed yellow monoclinic needles.

Ammonium dioxalatoplatinate(II) $(NH_4)_2Pt(C_2O_4)$. This salt was prepared similar to the K salt, using $(NH_4)_2PtCl_6$ and $(NH_4)_2C_2O_4 \cdot H_2O$. It is a white ppt, insoluble in all the common solvents such as water, acids, alcohol, ethers and acetane. Thus, we have not been able to recrystallize the crude product.

Lithium dioxalatoplatinate(II) $Li_2Pt(C_2O_4)_2$. Attempts to synthesize $Li_2C_2O_4 \cdot H_2O$ failed, probably because the reaction mixture was too acidic. It had a pH of 2 compared to the K solution (which precipitated $K_2Pt(C_2O_4)_2$) of a pH 7-8. Thus, the synthesis was repeated by first neutralizing H_2PtCl_6 with LiOH or Li_2CO_3 until a slightly basic solution resulted. Dark orange powder of $Li_2Pt(C_2O_4)_2$ was obtained and is extremely soluble in cold water.

Silver dioxalatoplatinate(II) $Ag_2Pt(C_2O_4)_2$. This yellow salt was obtained by adding a calculated amount of $AgNO_3$ to a hot solution of $K_2Pt(C_2O_4)_2$. It is very sensitive to light, and decomposes to give Ag.

$$Ag_2Pt^{II}(C_2O_4)_2 \xrightarrow{h\nu} 2Ag + [Pt^{IV}(C_2O_4)_2]^{\bullet}$$

The silver salt is very useful for the formation of other dioxalatoplatinates(II).

The acids $H_2Pt(C_2O_4)_2$. This acid was prepared by adding an equivalent amount of 2N HCl to the yellow $Ag_2Pt(C_2O_4)_2$. However, this dark blue solution is unstable, and is oxidized by air to give the Krogmann "violet" acid.

$$Ag_2Pt^{II}(C_2O_4)_2 + 2HCl \longrightarrow H_2Pt^{II}(C_2O_4)_2 + 2AgCl$$

$$H_2Pt^{II}(C_2O_4)_2 + O_2 \longrightarrow H_{1.6}[Pt^{II}_{0.8}\ Pt^{IV}_{0.6}\ (C_2O_4)_2]$$

In order to get the unoxidized acid, the reaction has to be carried out with exclusion of air and light. Attemt to isolate $H_2Pt(C_2O_4)_2$ or $H_{1-6}Pt(C_2O_4)_2$ has not been tried, as we are mainly interested in making the Krogmann salts from these acids.

Sodium dioxalatoplatinate(II) $Na_2Pt(C_2O_4)_2$. When a solution of NaCl was added to an equivalent amount of $Ag_2Pt(C_2O_4)_2$, a slight orange color was seen which disappeared instantaneously, and a dirty-grey ppt was formed. The ppt dissolved in warm water to give a yellow solution, and blue streaks were observed to start at the surface of the ppt and disappear into the solution. Finally, the dirty-grey ppt became white in color, resembling AgCl. (Could it be the Na salt is absorbed on the AgCl?) The yellow solution, which undoubtedly contained the Na salt, was then concentrated until an orange solution resulted. On cooling, it turned dark-green. After standing at room temperature overnight, very thin, dark brown, shiny needles were formed, together with some finely divided Pt metal. The needles resemble the $K_{1.6}Pt(C_2O_4)_2$. The $Na_2Pt(C_2O_4)_2$ solution must have been oxidized to the "violet" Krogmann complexes.

Magnesium dioxaletoplatinate(II) $MgPt(C_2O_4)_2$. The Mg salt is comparatively much more soluble than the K salt. It was prepared from either $K_2Pt(C_2O_4)_2$ or $Ag_2Pt(C_2O_4)_2$ by addition of aqueous $MgCl_2$.

Calcium dioxalatoplatinate(II) $CaPt(C_2O_4)_2$. This salt exists in several phases. When a cold solution of $Ca(NO_3)_2$ was added to a solution of $K_2Pt(C_2O_4)_2$, a yellowish-orange ppt was obtained. But when a hot solution of $Ca(NO_3)_2$ added to $K_2Pt(C_2O_4)_2$, the ppt formed was orange-red, which dissolved in hot water slowly to give a yellow solution and some red ppt. The yellow solution on cooling gave ppt of the first kind, ie. yellowish-orange in color. Recrystallization of the red ppt above 70°C gave very nice, shiny, dark red crystals, perhaps suggesting the extence of chain structures even in the unoxidized Ca salts.

Barium dioxalatoplatinate(II) $BaPt(C_2O_4)_2$. The reactions of $BaCO_3$ with $H_2Pt(C_2O_4)_2$ and $BaCl_2$ with $K_2Pt(C_2O_4)_2$ gave the unoxidized Ba salt. It is an amorphous powder, yellowish-green in color, and very insoluble in hot water.

"Violet" or partially oxidized "Krogmann salts" $K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$.

0.5g $K_2Pt(C_2O_4)_2 \cdot 2H_2O$ was dissolved in 10 ml H_2O at 70°C and 0.1 g K_2PtCl_6 was then added. The solution turned dark blue immediately and a voluminous, coppery, spongy mass was formed. It was cooled to room temperature and filtered. The K salt was obtained as a shiny, coppery sheet, probably because the ppt was so fine and feathery that they adhered strongly to one another.

The oxidation of $K_2Pt(C_2O_4)_2$ has also been carried out with dichromates, but was not very successful, contrary to what Krogmann reports. Failure of oxidation might be due to the wrong acidity of the solution. Since oxidation by K_2PtCl_6 was so convenient and easy, no further attempt on using dichromates has been made.

The oxidation of the yellow K salt has also been done by adding a few drops of concentrated H_2SO_4 to a hot, concentrated solution of $K_2Pt(C_2O_4)_2$. However, this method of oxidation tends to deposit finely divided Pt metal as well, and is therefore discarded.

The recrystallization of the "violet" K salt from hot water has been the most difficult step, and would be discussed later.

"Violet" acid $H_{1.6}Pt(C_2O_4)_2$. As we mentioned earlier, the "yellow" acid, $H_2Pt(C_2O_4)_2$, is not stable towards oxidation, and is immediately oxidized by air to give the "violet" acid. The concentrated solution of $H_{1.6}Pt(C_2O_4)_2$ is also blue-black. To get crystals of $H_{1.6}Pt(C_2O_4)_2$, the solution has to be dehydrated under vacuum, otherwise it will decompose to give Pt metal. Attempt to freeze-dry $H_{1.6}Pt(C_2O_4)_2$ has not been carried out, as the acid was used to obtain other "violet" salts as soon as it was made.

"Violet" Na, Mg, Ca Salts. All these salts have been prepared in a manner similar to the method for obtaining the K salt, ie. by oxidizing the corresponding "yellow" salts with K_2PtCl_6. They are deeply colored in powder form.

X-ray characterization. Powder patterns of both the "yellow" and the "violet" K&Mg salts were run at CMR, and also recorded photographically by Ted Hopkins. The photographs were taken using a Weissenberg camera (with a diameter of 60.1 mm), Cu radiation with a Ni filter, and with exposure times of about two hours. The samples were ground from the parent crystals, and "vibrated" into thin-walled capillaries with a diameter of about 0.3 mm.

Attempts to produce single-crystals of the "violet" salts. Most of our work was done on the K salts, since they are comparatively easier to prepare.

(1) Attempted transformation of yellow crystals to violet form. It was found that on adding a solution of warm K_2PtCl_6 to solid $K_2Pt(C_2O_4)_2 \cdot 2H_2O$ the yellow color of the oxalato complex gradually changed through dark green to dark brown with a metallic sheen, resembling the "violet" K salts obtained by the oxidation of solid K_2PtCl_6 on solution of $K_2Pt(C_2O_4)_2$. If the end product was indeed pure $K_{1.6}Pt(C_2O_4)_2$, then this method of oxidation would provide us a quicker and much easier way of obtaining large, single crystals of the "violet" salt. However, the powder pattern of a sample of the "violet" salt made this way was run, and indicated the oxidation did not go to completion. An experiment was then set up to follow the path of oxidation by this method. Two crystals of $K_2Pt(C_2O_4)_2$ were investigated. Oscillation photographs were taken of the original crystals and the course of the oxidation was followed by further photographs, oscillating

around the same axes each time. It was found that the single crystal pattern of the starting crystals gradually disappeared, and the powder pattern of the "violet" salt began to appear. The origin of this powder pattern can be visualized as arising from a collection of very small crystallites oriented in a completely random fashion. Even after more than one hour's oxidation time, there is still a distinctly visible trace of the original single crystal pattern of the starting crystal, although there is evidence of preferred orientation of the small crystallites.

The failure of oxidizing solid $K_2Pt(C_2O_4)_2$ by solution of K_2PtCl_6 is not unexpected though. In the yellow salt, there are no chains. The distance between the nearest Pt is 7.68 Å. Of course, there is no possibility for an interaction here. But in the "violet" salt, the Pt-Pt distance is 2.85 Å. Thus, in the transformation of yellow crystals to the "violet" form, there is a tremendous shrinkage of more than 60% in the Pt-Pt distance. This obviously proves too big a change, and as a result, the single crystal just breaks up into many tiny crystallites.

2. From crude product of $K_{1.6}Pt(C_2O_4)_2$ obtained from the oxidation of solution of $K_2Pt(C_2O_4)_2$ by solid K_2PtCl_6. The crude product of the "violet" salt was recrystallized repeatedly from hot water. But crystals of these violet salts tend to from extremely thin filaments of the order of millimeters in length and microns in diameter. (The corresponding Mg, Ca and Na salts are even smaller). They have the general appearance of copper-colored "hair", the corresponding

Mg, Ca and Na salts are a bit darker in color and not as shiny as the K salt.

Attempts to grow bigger crystals in a H-tube using temperature-gradient-diffusion technique were not very successful. The crystals that were formed were still "hair" and were extremely difficult to separate and remove out of the solution.

Some of the K crystals appeared much thicker, e.g. 0.1 to 0.2 mm in diameter and 1 to 2 mm in length. However, the first such crystals which were examined proved to be multiple crystals, formed by bunches of the hair-like filaments, aligned nearly in the same way. In the case of the "violet" K (and also the Mg) salt, after several recrystallizations in a test-tube, the formation of the extremely hair-like filaments seems to be slightly inhibited. Some of the larger crystals are single. From the oscillation photographs of such a single crystal (0.5 mm x 0.2 mm x 0.05 mm), the Pt-Pt distance was formed to be 2.85 Å, in excellent agreement with Krogmann's report.[8] The K salt was also found to be triclinic.

The densities of the "violet" K salts were measured, but there seems to be a difference between the densities of the very finest needles and the layer crystals. Possibly, the size difference has some effect on the density discrepency.

Micro-analysis and IR spectrum indicated there is no chloride present in the "violet" salt showing there is no ligand exchange during the oxidation with K_2PtCl_6.

(3) $Mg_{0.82}Pt(C_2O_4)_2 \cdot X H_2O$. No analysis on the crystals has been done, thus, the amount of water of crystallization is unknown. The Mg salt is the only one, other than the K salt) that we have had success in growing bigger single crystals by repeated recrystallization of the powder form at 30°. A Weissenberg photograph was taken from which it was found that the Mg "violet" salt has a hexagonal structure, with a Pt-Pt distance of 2.87 Å. The crystals again are very thin and long, like the corresponding K salt, but not so coppery in color, and they also polarize light. Although the crystal structure does not agree with any of the three phases that Krogmann reports,[10] (ie. $Mg_{0.82}Pt(C_2O_4)_2 \cdot 5.3 H_2O$ orthorhombic), the Pt-Pt distance is in fairly good agreement (2.85, 2.84, and 2.84 Å respectively). The different crystal structures of the three phases reported by Krogmann might perhaps be due to the different amounts of water of crystallization in them, and in our case, we might have formed a new phase of the Mg salt, pending on the number of water of crystallization. But the short Pt-Pt distance, coupled with the many similar behaviors to the "violet" K salt, clearly indicates that there is a metal-metal interaction and the compound in question is, no doubt, a "Krogmann salt."

Properties of "violet" salts. The powder form of the "violet" salts is always deep color (from dark brown to deep violet) and larger crystals always have a coppery sheen (due to polarized spectral reflection), independent of the cations. The solutions are always yellow when hot

or diluted, and on cooling, the color changes through orange, dark green, brown, purple to deep-blue.

The violet salts are less soluble in water than their corresponding unoxidized compounds.

Effect of acid on the polymerization of "violet" salts. Concentrated solutions of these "violet" salts are always blue-black, whereas the diluted solutions are pale-yellow, with a weak absorbency at 400 mm. It is suggested by Krogmann that disproportionation invariably occurs in solution. The depolymerization is thought to occur in steps:

$$[Pt^{II}_{0.8}\ Pt^{IV}_{0.6}\ (C_2O_4)_2]_n^{1-bn} \rightleftharpoons 0.8n[Pt^{II}(C_2O_4)_2]^{2-} + 0.2\ n[Pt^{IV}(C_2O_4)_2]^{\cdot}$$

The Pt^{IV} complexes complete their coordination by addition of water, from which H^+ can finally be removed.

$$[Pt^{IV}(C_2O_4)_2]^{\cdot} + 2H_2O \rightleftharpoons [Pt^{IV}(C_2O_4)_2(H_2O)_2]^{\cdot}$$

$$[Pt^{IV}(C_2O_4)_2(H_2O)_2]^{\cdot} \rightleftharpoons [Pt^{IV}(C_2O_4)_2(OH)_2]^{2-} + 2H^+$$

The removal of the H^+ from Pt^{IV} complex is suppressed by addition of acid, which thus forms the removal of H_2O and hence also polymerization. Very nice, larger, single crystals of the K salt have been obtained by adding a few drops of conc. H_2SO_4 to a hot, concentrated solution of the crude product $K_{1.6}Pt(C_2O_4)_2$, which changed from a deep brown color

to dark blue immediately. This undoubtedly pushes the above equilibrium towards the left, thus favoring the formation of the partially oxidized salts.

As the removal of H_2O seems essential for the polymerization, we thought that perhaps if we can recrystallize the "violet" salt in a nonaqueous but still quite polar solvent, e.g. dimethylformamide, we might be able to get good, big, single crystals. However, the attempt was unsuccessful. Similarly, attempts to get the corresponding Ca and Mg salts by addition of conc H_2SO_4 did not yield good crystals.

Attempts of introducing large cations into the oxalato complexes of Pt.

(1) $(CH_3)_4N^+Cl^-$ + $K_2Pt(C_2O_4)_2$: Unsuccessful, we got a yellow solution.

(2) With tetrabutylammonium iodide. An equivalent amount of tetrabutylammonium iodide (white, shiny flakes) in warm water was added to a warm solution of $K_2Pt(C_2O_4)_2$, no obvious change took place. However, on warming at 60°, the yellow solution turned cloudy. After standing at room temperature for a few days, dark green amorphous ppt was formed. No analysis has been done yet.

(3) With SALEN. When an ethanolic solution of SALEN was added to an aqueous solution of K_2PtCl_4, and the resulting solution warmed, the reactants separated out.

(4) With $Pt(NH_3)_4Cl_2$. $K_2Pt(C_2O_4)_2$ and $Pt(NH_3)_4Cl_2$ were mixed in order to get a compound analogous to the magnus green salt,

but with the formulat $[Pt(NH_3)_4][Pt(C_2O_4)_2]$. However, we got a creamy-white, very fine ppt. We would expect to see a darker-colored ppt, if there is a metal-metal interaction in the compound we hoped to make. Perhaps, the size of the oxalto ion is too big for chains of metal atoms to stack on one another.

(5) With 1, 1'-diethyl-2, 2'-cyanine chloride. The cyanine dye was added to $Ag_2Pt(C_2O_4)_2$ and $K_2Pt(C_2O_4)_2$ in order to find out if the compound $dye_2\ Pt(C_2O_4)_2$ would be formed. However, no AgCl was formed and there was no apparent reaction.

(6) With (CH_3)-$\emptyset_3P^+Br^-$. When a solution of $(CH_3)\emptyset_3P^+Br^-$ was added to a solution of $K_2Pt(C_2O_4)_2$, there was no visible change in the yellow solution. After standing overnight, the $K_2Pt(C_2O_4)_2$ separated out.

Again, when we added $(CH_3)\emptyset_3P^+Br^-$ to yellow $Ag_2Pt(C_2O_4)_2$, no AgBr was formed as anticipated.

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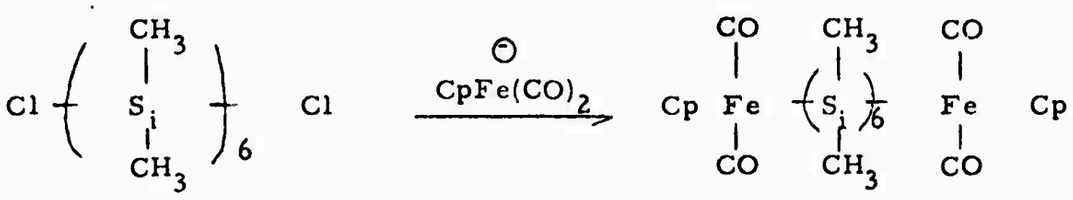
SYNTHESIS OF GROUP IV CHAIN COMPOUNDS

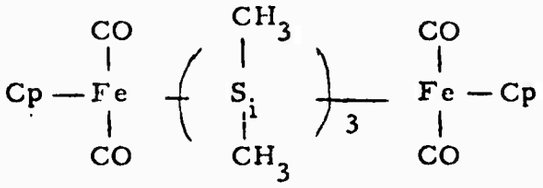
Manning P. Cooke, Jr.

This section of the report will describe experiments directed toward the preparation of chain compounds of silicon and germanium of potential importance as materials possessing unusual electrical properties. The general background to this problem has been previously reviewed[1] as has the subject of Group IV chain compounds.[2]

Initial efforts were directed towards the preparation of derivatives of hexasilane since the dichlorododecamethyl silane 1 is readily available.[3] The recent preparation of transition metal-capped derivatives of permethylsilanes[4] such as 3 prompted an attempt to prepare the analogous hexasilane derivative 2. Treatment of a THF solution of Cp-iron carbonyl anion with excess chloride 1 gave, after



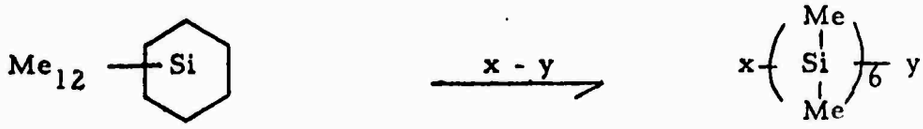
1 2



3

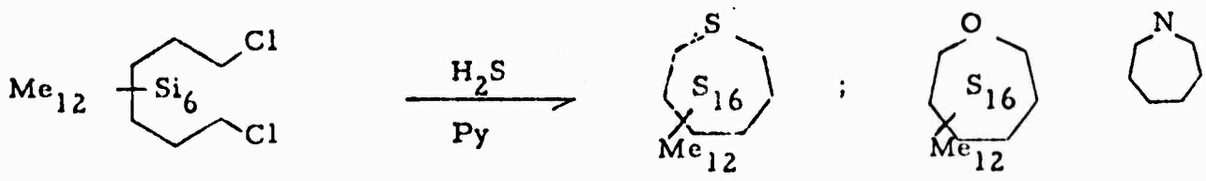
careful chromatography, trace amounts of a yellow air-sensitive compound suspected of being the desired derivative 2 possessing IR bands at 1995, and 1790 cm^{-1} (carbonyl) and 1409 and 1245 cm^{-1} (silyl methyl). This unstable compound was not further characterized owing to repeated failures to produce more than trace amounts. It seems likely from results to be discussed later that the very low yield here obtained results from the deleterious effects of strong nucleophiles on extended Group IV chains.

Attempts were then made to effect the cleavage of the readily available cyclic hexasilane 4 in hopes of preparing unsymmetrically substituted acyclic silanes such as 5 which could be coupled at one end selectively and then further functionallized. The hexamer was found to be generally inert to electrophilic cleavage by agents such as m-chloroperbenzoic acid and cyanogen bromide. 4 was consumed slowly by



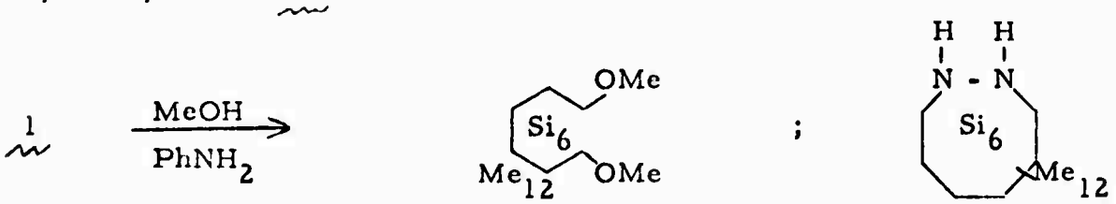
4 5

iodine and by cyanogen bromide in the presence of boron trifluoride etherate but in neither case could products be detected by glpc. Attempts to cleave the cyclic oxide 7 have been described.[1b] An attempt was made to prepare the corresponding cyclic sulfide 7 in hopes that it might



1 6 7 8

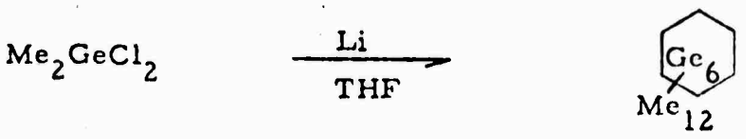
be more readily cleaved, however, only the oxide 7 could be obtained. Either the sulfide is readily hydrolized to the oxide or the initial silyl chloride-amine complex does not react with hydrogen sulfide as with lower silyl homologs. The hydrolytically unstable cyclic amine 8 could apparently be prepared in situ by treatment of 1 with aniline followed by ammonia. Treatment of this intermediate (visible by vpc) with hydrogen sulfide resulted in the disappearance of 8 without production of a product of comparable retention time. A product of longer retention time suggestive of the acyclic disufhydril derivative was observed but disappeared upon attempted workup. Treatment of 1 with methanol containing aniline readily gave the dimethoxy derivative 9 (see reference 16). This derivative was not stable to chromatography. Attempts to prepare the cyclic hydrazine 10 were likewise unsuccessful.



9 10

In anticipation of the ultimate necessity of coupling any multimetal unit in order to obtain chains we decided that germanium should be employed both because of its greater resemblance to tin for which satisfactory methods for metal-metal bond formation exist[5] and because of its tendency to form stronger bonds to other transition metals in general. The known permethylcyclohexagermane 11 seemed especially attractive in that simple ring cleavage would give a useful hexagermane fragment. The literature preparation of 11 from dimethylgermanium

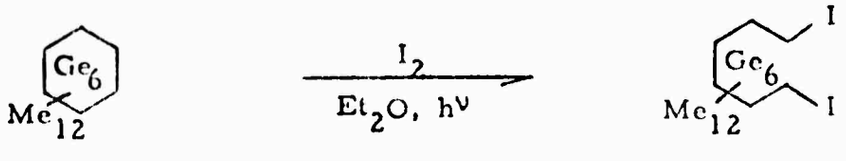
dichloride was not easily reproduced, however, and a large number of different products could be discerned by vpc depending on the detailed



11

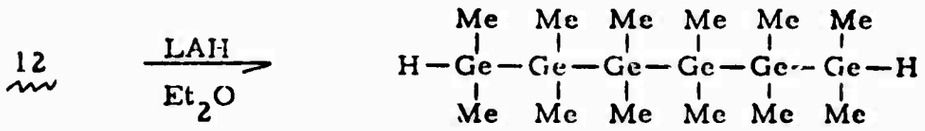
procedure and workup employed. A number of these side products were collected by preparative vpc but their structures were not firmly established. Nmr data suggested that most were polygermane halides. An exact procedure was developed for the preparation of 11, however, allowing this material to be obtained in 24% yield with careful attention to the exact procedure.

The simple cleavage of 11 was then studied and it was found that under very carefully controlled and exact conditions 11 could be cleaved by iodine in THF in the presence of light to give a solution of hydrolytically unstable di-iodide 12. The resulting di-iodide was not isolatable nor observable by vpc but could be converted into more stable isolable derivatives. It was found that slow addition of iodine to a solution of 11 under diffuse light gave the best results. Iodine uptake is much faster under stronger light (sunlight) but at the expense of decreased selectivity resulting in the generation of smaller chain fragments. The reaction was inhibited by the presence of metals and it was found that the iodine could not



11 12

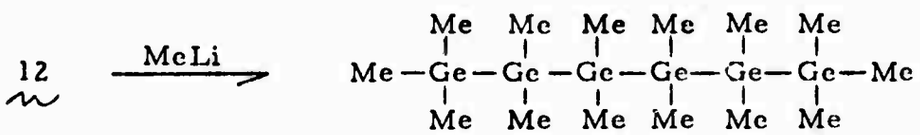
be handled with metallic tools. The iodine should be handled with a glass spatula and a glass encased stirring bar used. Immediate reduction of 12 with lithium aluminum hydride gave the dihydride 13 which was



13

purified by preparative vpc. The dihydride is not stable over long periods in air (2 days) and stable for only short periods in solution in the presence of air. The dihydride is immediately destroyed by chlorosolvents.

Treatment of di-iodide 12 with excess methyllithium gave the permethylhexagermane 14 which was easily purified by preparative vpc. The permethyl derivative is obtained in approximately 60% yield



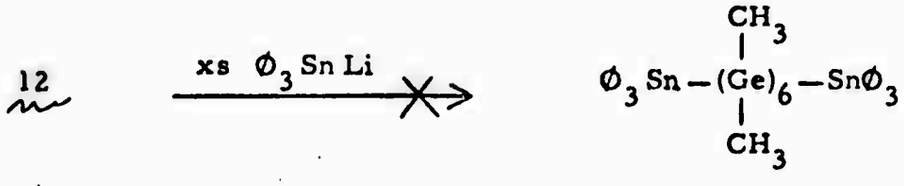
14

as estimated by vpc analysis thus established a lower limit on the yield of the iodine cleavage. Interestingly, a crystalline inclusion complex was obtained by shaking 14 with a saturated thiourea solution.

Treatment of 12 with phenyllithium (excess) did not give the desired

15

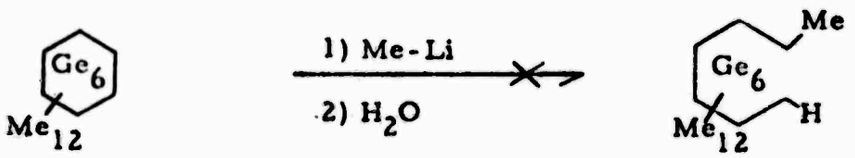
derivative,[15] however, and analysis of the reaction mixture by NMR showed the presence of many different kinds of methyl germane signals indicating extensive fragmentation or cleavage of the germane chain. This behavior is not surprising since it is known that nucleophiles -- especially lithium reagents[7,8,9] cleave polygermane chains. Even nucleophiles such as potassium ethoxide cleave polygermanes in HMPA.[10] It seems likely that the diphenyl derivative could be prepared if care were taken to prevent an excess of the lithium reagent. An attempt to prepare the triphenyltin derivative 16 through treatment of 12 with triphenyltin lithium was likewise unsuccessful in that nmr analysis



of the product obtained indicated the presence of a number of triphenyltin polygermanes. Again, a pure product could likely be obtained by

avoiding the presence of excess lithium reagent--a task made difficult by the inability to know the exact amount of 12 present.

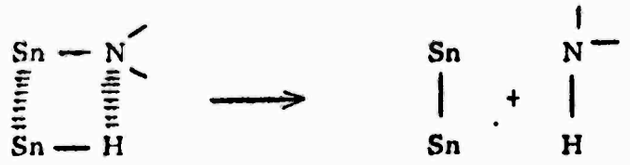
An attempt to make use of the cleavage reaction by treating the cyclic germane 11 with nucleophiles such as methyllithium, or phenyllithium in HMPA was unsuccessful.



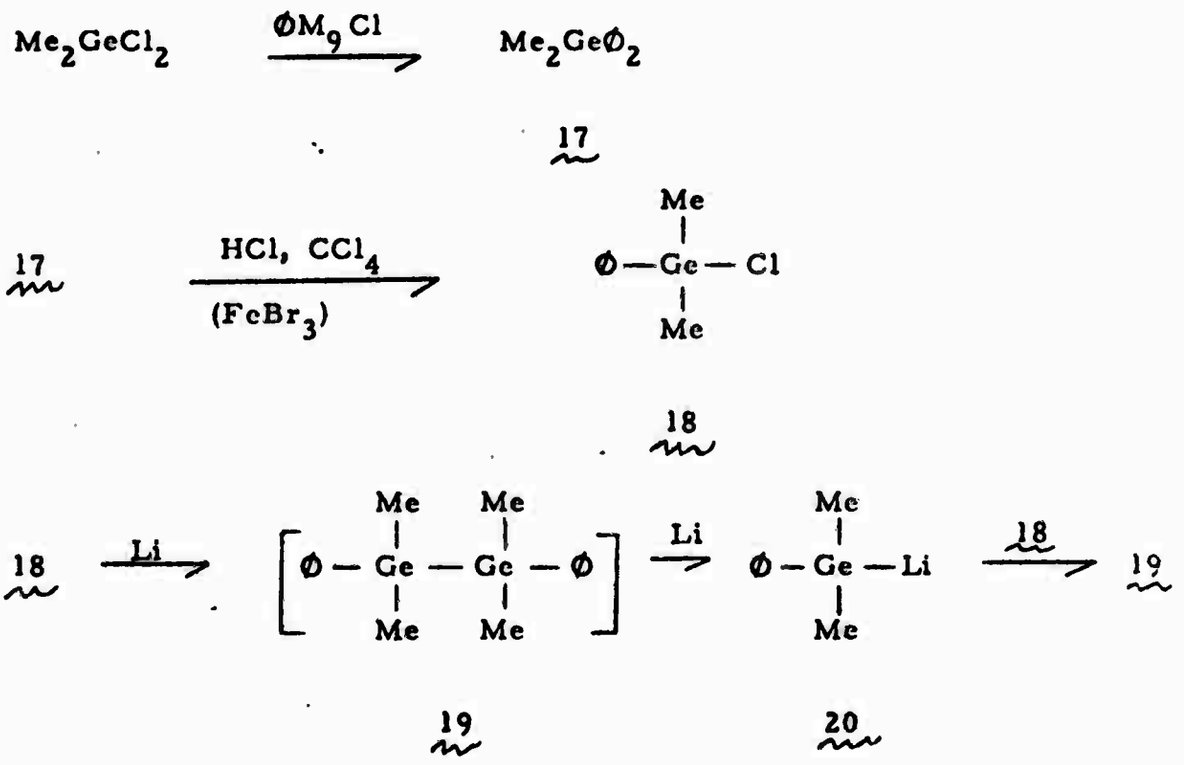
11

The cyclic germane is rapidly consumed in this media giving many smaller fragments resulting from extensive disproportionation. It is amusing in retrospect that excess methyl lithium in ether gives cleanly 14 without disruption of the chain.

Having the potentially useful di-iodide in hand, consideration was given to methods of making germanium-germanium bonds in order that the hexamer units might be coupled. Owing to the cleavability of polygermanes by anions, coupling methods (Wurtz type) proceeding via germanium anions are not useful for the preparation of longer chains. Likewise, the excellent methods available for tin-tin formation (the coupling of tin amides with tin hydrides) are in general not useful with germanes.[11] It would seem, however, that the presence of similar

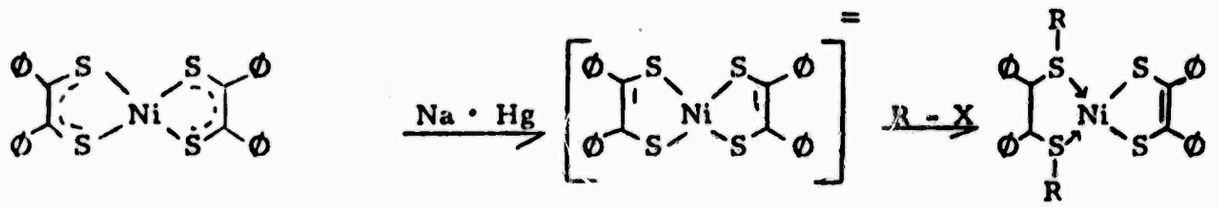


d-orbitals in germanium might allow bond formation to occur through a similar type of front-side, four center mechanism. In order to develop a useful coupling method, a simple chlorogermane, 18, was prepared essentially by the literature method[9] outlined below. The chlorinative



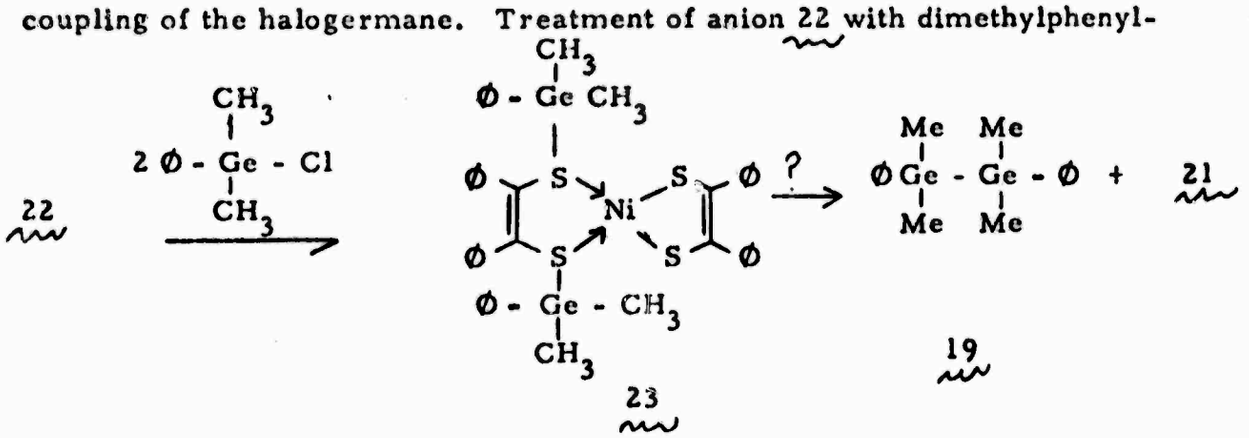
dephenylation of 17 was found better effected using the milder ferric bromide as catylyst rather than aluminum chloride. The digermane 19 which would result from successful coupling of the monogermane 18 was prepared via the useful lithium derivative 20.

The first idea for metal-metal bond formation tested involved the use of metal dithienes.[12] Metal dithienes such as 21 are readily reduced to anions in which the excess charge resides mostly on the sulfur atoms giving rise to s-alkylation when treated with electrophiles. It seemed possible that such a system might hold two germanium moieties

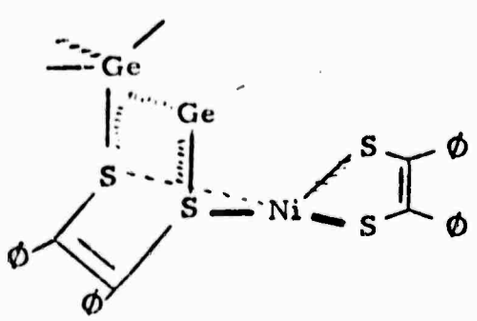


21 22

in such a way as to allow bond rearrangement giving net reductive coupling of the halogermane. Treatment of anion 22 with dimethylphenyl-



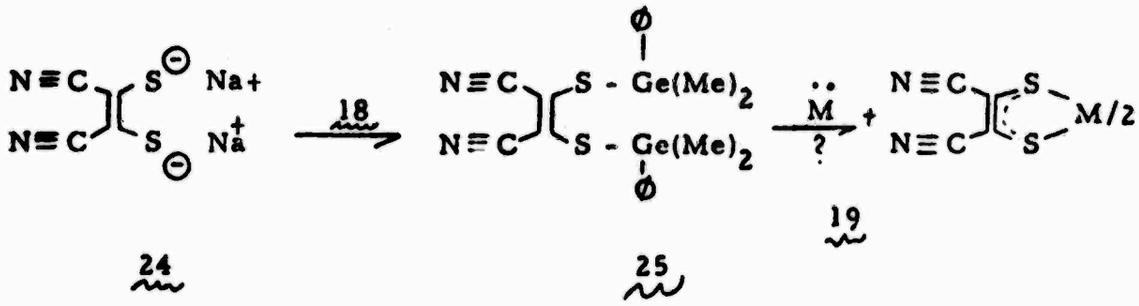
23 19



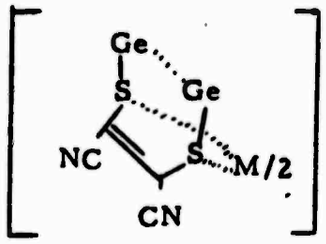
23

germanium chloride 18 failed to give any digermane 19 (vpc). It seemed likely that the intermediate germane 23 was stable towards the desired fragmentation but neither heat nor ultraviolet irradiation forced the desired transformation.

A variation of this idea also pursued involved preparation of the

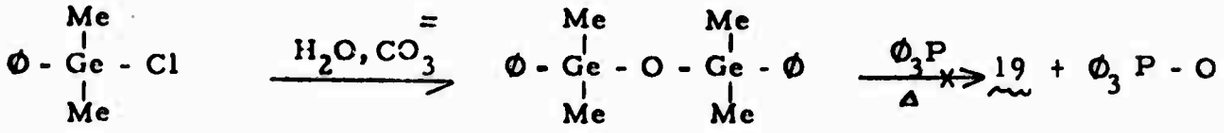


24 25 19



dimercaptomaleonitrile derivative 25 in situ (acetonitrile) by the treatment of 24 (see Report, R. Stark) with chlorogermane 19 in hopes that a reducing metal capable of forming a very stable dithiene complex might effect a reductive extrusion of the dithiene ligand with concomitant digermane formation. While 25 was not isolated, its presence was indicated by a sharp resonance at 47 cps. Treatment of a solution presumed to contain 25 with iron pentacarbonyl resulted in immediate evolution of carbon monoxide but the desired digermane could not be detected by vpc.

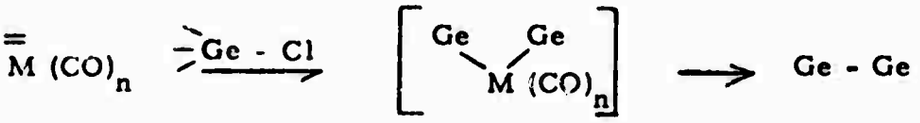
Another approach briefly examined was that of heteroatom extrusion. Treatment of the oxide 26 (prepared by hydrolysis of the



18 26

chloride 18) with triphenyl or tributyl phosphine under a variety of conditions (fusion at 250°, 100° in HMPA etc.) failed to give any digermane or phosphine oxide. The more promising extrusion of sulfur from the corresponding sulfide with a phosphorous triamide should probably be tried.

The last method briefly examined involved the principle of reductive elimination of groups attached to metal carbonyls.



It was hoped that treatment of a metal carbonyl dianion with a germanium halide might give an intermediate which would expel the desired digermane. When both the iron tetracarbonyl dianion 27 and the chromium pentacarbonyl dianion 28 were treated with the chlorogermane 18, no digermane resulted. All attempts to provoke the reductive

elimination of any stable intermediate (heat, light, added ligand such as triphenylphosphine) failed. It seems likely that the intermediates contain metal-metal bonds of sufficient strength such as to prevent the required reductive elimination of the desired digermane. R. Stark continues in this general area.

EXPERIMENTAL

Unless otherwise noted, all gas chromatograms were obtained using a 10' 10% UCW-98 silicon column at a flow rate of 80 cc/min He. Preparative glpc was performed by inserting a glass tube in the outlet port cooling the tube with dry ice chips when necessary. Nmr values are reported in cps from tetramethylsilane.

Dodecamethylcyclohexagermane,11. - - The literature procedure[6] for the preparation of this compound could not be reproduced in our hands and the following procedure was developed. The isolation and purification of the product is difficult and careful attention to this aspect is urged.

In a dried flask under argon was placed 0.90g of lithuim metal chips prepared by cutting a 10 cm chip of lithium ribbon (0.089g/cm, Foote Mineral Co.) into small pieces approximately 3 mm x 3 mm. The petroleum jelly coating was removed by washing twice with small volumes of hexane decanted with the aid of a syringe. The lithium was then suspended in 9 ml dry THF. With vigorous magnetic stirring there was added 2.0 ml (17.2 mmole) of neat dimethylgermanium dichloride over 2.hr. at a bath temperature of 50-55°. The reaction was initiated by applying the first drops of dichloride directly on top of the quietly floating lithium chips thereby causing the activation of the otherwise tarnished surface. This process required but several minutes whereupon stirring could be commenced with addition of the bulk of the dichloride. The mixture was cooled, diluted with several volumes of

of ether, filtered to remove the excess lithium and the resulting solution evaporated to dryness. The resulting residue was extracted with hexane and the soluble fraction passed through a 2-inch plug of silicic acid (Baker) to remove polymers and germanium halides. The oil thus obtained (1.10g) was dissolved in acetone and treated with water until near the cloud point and then allowed to stand overnight at 4° (refrigerator). In this way there was obtained 420 mg (24%) of pure 11 (first crop).

vpc: 230°, Tr~ 5.1 min.

nmr: CCl_4, 21 cps (singlet)

mass spec.: M^+ observed. (The presence of natural Ge isotopes makes exact pin pointing of the parent ion difficult without computer analysis and the parent ion was considered confirmed if the mass cluster centered within several units of the computed molecular weight.

Vpc analysis of the crude reaction product showed the presence of a more volatile product (Tr ~2.4 min.) which was collected by prep vpc and shown to be the cyclic pentamer decamethylcyclopentagermane, nmr 20 cps.

Present results of Rex Stark suggest that this preparation is improved by the use of lithium metal containing 1% sodium.

Cleavage of 11 with Iodine. Preparation of Di-iodide 12. Careful attention to this procedure is required (see discussion section). Into a small serum-capped vial containing a small glass covered magnetic

stirring bar was placed 62 mg (0.10 mmole) of hexamer 11 and 1.0 - 1.5 ml dry ether best introduced by needle stock syphon from a virgin, serum capped ether can. Solid iodine, 28 mg (weighed and handled via a glass spatula) was added in four portions, waiting until the iodine color was discharged under the influence of ordinary room light before a new portion was added. After the last portion of iodine was consumed, the solution was found from subsequent trapping experiments to contain the di-iodide 12 produced in approximately 60% yield. The iodide was not isolated and is not visible by vpc and this solution was used directly for the subsequent preparations. The presence of trace amounts of metals introduced by handling the iodine with a "stainless" spatula or from small iron filings clinging to ordinary stirring bars greatly inhibited to reaction.

Dihydride 13. - - A solution of the above di-iodide 12 obtained from the cleavage of 62 mg (0.1 mmole) of 11 was transferred by needle syphon to a vial containing excess lithium aluminum hydride (~100 mg) in 2 ml dry ether. The mixture was stirred at room temperature 1 hour and the excess hydride destroyed by the careful addition of water. The ether phase was separated from solids and washed with several portions of water, dried over sodium sulfate and evaporated in a stream of nitrogen. Preparative vpc gave 15 mg of the dihydride 13 as an oil which is rapidly decomposed by halosolvents and slowly decomposes upon standing in air and especially in solutions exposed to air. An acceptable analysis

was not obtained, probably owing to slight decomposition during preparative vpc collection. The compound appeared pure by nmr and its structure was unambiguously established by nmr and mass spectroscopy.

vpc: 220°, immediately after the starting material 11.

nmr: benzene-d_6, 22.5 cps (doublet, J = 4) α - CH_3^5

27.5 (singlet) β - CH_3^5

29.5 (singlet) γ - CH_3^5

24.5 (heptet) terminal H

Analyzed for $C_{12}H_{38}Ge_6$ (617.977), 23.32%C; 6.20%H; Found: 24.56%C, 6.27%H.

Tetradecamethylhexagermane 14. - - A solution of the di-iodide 12 from the cleavage of 62 mg (0.10 mmole) of 11 was treated with excess methyl lithium solution (Foote) and stirred for 0.25 hr. at room temperature. The ether solution was washed with water, dried over sodium sulfate and concentrated. Purification by preparative vpc gave pure 14 as an oil. A yield of 60% was estimated by vpc analysis using a weighed amount of added hexamer 11.

Anal. for $C_{14}H_{42}Ge_6$: 26.03%C, 6.55%H; Found: 26.31% C, 6.55% H.

vpc: 220°, Tr 4.5 min.

nmr: benzene-d_6; 20.5 cps (singlet) terminal CH_3^5

27.5 cps (singlet) β - CH_3

30.0 cps (singlet) γ - CH_3

Dimethyldiphenylgermane 17. - - This compound was prepared by the literature procedure.[19] A solution containing 17.36 g (11.7 ml, 0.10 mole) dimethylgermanium dichloride in 300 ml THF was treated with 75 ml of 3M phenylmagnesium chloride solution (Arapahoe). The mixture was cooled by a water bath during the addition. The mixture was stirred at 50° for 1 hour then at room temperature for 2 hours. The thick mixture was diluted with ether, poured into water containing a small amount of ammonium chloride to dissolve all salts and extracted twice with ether. The oil obtained after drying gave upon distillation 22.1g (86%) of pure 17, bp 102°(1.5mm) (lit.[19] bp 125-126 (3mm)).

nmr: CCl_4; 36 cps (s), 437 cps (m).

vpc: 180°, Tr 2.3 min. (6.5 foot SE - 30).

Chlorodimethylphenylgermane 18. - - This compound was prepared by a modification of the literature procedure.[9] In a 250 ml side-arm flask equipped with a drying tube was placed 12.85g (0.05 mole) of 17, 100 ml of CCl_4 and 100 mg of anhydrous ferric bromide. Hydrogen chloride was passed through the solution by means of an inlet tube (disposable pipet) inserted through the side-arm. Samples were periodically withdrawn and analyzed by vpc (column 180°) until all starting material had been consumed whereupon the reaction solution was ebullated with nitrogen to remove excess hydrogen chloride. The solvent was removed under reduced pressure and upon distillation of the residual oil there was obtained 8.75 g (82%) of 18, bp 106-107% (14 mm) (lit[9] bp 110-112° (24 mm)).

vpc: 180°, Tr$\sim$0.8 min.

nmr: CCl_4, 52 cps (s), methyl, 443 cps(m), phenyl.

Dimethylphenylgermanyl lithium 20. - - In a dry 25 ml flask (argon, glass magnetic stirring bar) was placed lithium chips prepared from 15 cm (0.2 mole) of lithium ribbon. The lithium was washed twice with hexane and then suspended in 12 ml of dry THF. There was added with stirring 3.0 g (0.014 mole) of 18 in 3 ml THF over 0.25 hr. A vigorous reaction ensued--the solution becoming suddenly dark green after a few minutes. (The colorless digermane 19 is first formed and then after all chloride has been consumed the colored lithium reagent is formed by reductive cleavage of 19.) The mixture was stirred for 1.5 hr.

1,1,2,2--Tetramethyl-1,2-diphenyldigermane 19. --To a solution containing 3.0 g (0.014 mole) of 18 was added the above solution of lithium derivative 20 transferred away from the excess lithium by means of a needle stock syphon. The color was immediately discharged. The colorless solution was then treated with a single chip of lithium metal to effect the exact conversion of all chloride to digermane. (The end point is signalled by a sudden coloration whereupon the lithium chip is removed). The solution was evaporated and distillation of the residual oil gave 4.58 g (91%) of 19, bp 111-113° (0.3 mm) (lit.[9] bp 162° (8mm)).

vpc: 182°, Tr 5.2 min.

nmr: CCl_4; 28 cps(s), 435 cps (m).

Nickel Dithiolate 23. - - The literature method[17] was modified. A mixture containing 10 g of benzoin, 70 ml of dioxane and 20 g of P_2S_5 was held at reflux during 5 hr. To the cooled solution was added

5.0 g of nickel chloride hexahydrate in 20 ml of water and the mixture heated on steam for 3 hr. Cooling gave 2.5 g of 23 as green-black needles after filtration and washing with two small portions of dioxane.

Dianion 22. - - Dianion 22 was prepared by the reduction of 23 with 1% sodium amalgam in THF. A solution of 270 mg (0.5 mmole) of 23 in 8 ml THF was reduced over 1 ml of 1% amalgam under nitrogen. The yellow-brown solution was used directly. Treatment of the dianion with both trimethylsilyl chloride and germanyl chloride 18 under a variety of conditions (see Discussion) did not result in metal-metal coupling.

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PRELIMINARY STUDIES OF Ge-Ge COUPLING REACTIONS

Rex Stark

During this period, I began a systematic investigation of the practical aspects of preparing and utilizing simple organogermanes, and attempts were made to improve on work by Kumada, Sakamoto, and Ishikawa.[1] All compounds prepared were standardized on the gas chromatograph.[2]

The coupling reaction to form a Ge-Ge bond investigated by earlier workers[1] was found to be satisfactory; i.e., reacting phenyldimethylgemyllithium with a chlorogermane in THF. Further work will be needed to maximize yields of the required chlorogermanes, which are prepared by hydrochlorodephenylation of phenyl-substituted germanes with dry HCl using $AlCl_3$ or $FeBr_3$ as a catalyst in one of several solvents (THF, $CHCl_3$ CCl_4). In several instances my yields were significantly less than those previously reported, and even the best yields reported for some of the reactions leave much to be desired.

The reactions employed thus far in these syntheses were as follows:

$$Me_2GeCl_2 \xrightarrow[THF]{\emptyset MgCl} \emptyset_2GeMe_2 \qquad (1)$$

$$\emptyset_2GeMe_2 \xrightarrow[CCl_4]{HCl\ FeBr_3} \emptyset GeMe_2Cl \qquad (2)$$

$$\emptyset GeMe_2Cl \xrightarrow[THF]{Li} \emptyset GeMe_2Li \xrightarrow{\emptyset GeMe_2Cl} \emptyset(GeMe_2)_2\emptyset \qquad (3)$$

$$\emptyset(GeMe_2)_2\emptyset \xrightarrow[\text{catalyst}\ \text{solvent}]{HCl} \emptyset(GeMe_2)_2Cl \qquad (4)$$

$$\emptyset GeMe_2Cl \xrightarrow[Na_2CO_3]{H_2O} \emptyset GeMe_2OH \longrightarrow \emptyset Ge(Me)_2\text{-}O\text{-}Ge(Me)_2\emptyset \qquad (5)$$

No serious problems were encountered prior to the dephenylation of the digermane, which has been the most difficult reaction studied to date. Worthy of mention also is the fact that an impurity was formed in the first reaction which persisted in small amounts throughout each of the succeeding reactions, being unreactive toward H_2O, lithium metal, and HCl in the presence of a catalyst. The concentration of this impurity was found to increase at times during the dephenylation reaction (4). This compound has not yet been isolated and identified, but has been shown by VPC to be distinguishable from each of the compounds in the above reaction scheme.

Preparation of Dimethyldiphenylgermane

8.68 gm (5.85 ml, .05 mole) Me_2GeCl_2 in 150cc dry THF was treated with 45cc $\emptyset$MgCl, 2.5M in THF. The exothermic reaction was cooled in an ice bath. After all the $\emptyset$MgCl was added (~ 5 min.) the mixture was stirred at room temperature for two hours. The mixture was

diluted with ether and then poured into ~ 50 cc H_2O containing enough NH_4Cl to dissolve all the precipitates. The solution was then extracted twice with Et_2O and the ether layers were washed with water, sat. NaCl, and dried over Na_2SO_4. Distil product 130 - 134° C. (3.2 mm). Yield 9.25 gm (72%).

Repeat above using 9.8 cc (.084 mole) Me_2GeCl_2 in 300 cc THF, adding 76 cc ØMgCl. No precipitates formed upon completion of the reaction, but the mixture became turbid when poured into H_2O. Product distils 121-128° (1 mm), of questionable purity. Identical by ir and nmr to first batch. Yield 14.30 gm (66.2%).

Repeat using 11.7 ml (17.4 gm, .1 mole) Me_2GeCl_2 with 90 cc ØMgCl. Accidentally heat to reflux for~ 15 min., then follow above procedure. Product distils 123-128° (1 mm). A cloudy, high-backing fraction distilled at 132-136° (.7mm). Product better than 95% pure by VPC. Yield 20.3 gm (79%).

A lower boiling (shorter retention time) impurity was present in each of the above preparations.

Synthesis of Chlorodimethylphenylgermane

The procedure is a modification of that used by Kumada et. al.[1] Previous work by Manning Cooke had indicated that $AlCl_3$ was too strong a catalyst, causing some dichloride to form in the presence of excess gaseous HCl.

In a sidearm flask equipped with a drying tube is placed $Ø_2GeMe_2$ in CCl_4, with anhydrous $FeBr_3$ as a catalyst. Anhydrous HCl is bubbled through a tube in the sidearm. The reaction is monitored by removing small aliquots for injection into the gas chromatograph. After the starting material is all gone, the excess HCl is driven out with nitrogen. The solution is

evaporated to dryness and the product is distilled at reduced pressure.

1 gm (.00389 mole) ϕ_2GeMe_2 was placed in 15 cc C Cl_4 with 10-20 mg $FeBr_3$. After three hours of bubbling HCl through the solution, the starting material was still present to about 30%. More $FeBr_3$ was added and the HCl was increased. The starting material was consumed after an additional two hours.

12.85 gm (.05 mole) ϕ_2 $GeMe_2$ was placed in 100 cc C Cl_4 with a ~100 mg $FeBr_3$. After a half hour of bubbling HCl, the solution was saturated and left overnight. Then HCl was added for three hours longer and the solution left saturated overnight. The starting material was gone on the third day. The above 1 gm batch was added, the solvent stripped off, and the product distilled at 116-124°C (16 mm). Vpc showed all four fractions to have some of the impurity initially present in the ϕ_2GeMe_2, with the fourth fraction about 10-15% contaminated. The nmr was very good. Yield 9.90 gm (85.3%). The starting material was almost gone on the second day. More $FeBr_3$ was added and the solution was resaturated with HCl. All the starting material was gone on the third day. Distil product 116-124° (16 mm). Nmr and ir of the first two fractions were identical to the previous preparation. The small third fraction was impure and therefore discarded. Yield 5.97 gm (74.7%).

Repeat with 12.85 gm ϕ_2GeMe_2 in 100 cc C Cl_4 with ~1/2 gm $FeBr_3$. Starting material was consumed by the third day. Distil 116-126° (14 mm). All four fractions had some of the impurity from the ϕ_2GeMe_2, with the fourth fraction about 30% contaminated. Combine first three fractions for yield of 8.49 gm (79%). The fourth fraction was saved for isolation of the impurity.

Additional work on the synthesis of $\phi(GeMe_2)_2$ Cl indicates that it would be more advantageous (much less time consuming) to use a different solvent and/or catalyst and to add small amounts of HCl via a greased syringe rather than to bubble the gas through the solution. The $FeBr_3$ is only slightly soluble in CCl_4, with $CHCl_3$ being a much better solvent. $AlCl_3$ might be suitable as a catalyst after all, if the amount of HCl added is carefully monitored to avoid forming the dichloride.

Preparation of 1, 2-diphenyltetramethyldigermane

In a dry flask under argon is placed 20 cm Li ribbon (~1.8 gm, .26 mole) cut into small chips. Wash twice with hexane and decant (needle syphon). Add 15-20 cc dry THF and then while stirring add 4.0 gm (.0186 mole) $\phi GeMe_2Cl$ in 5cc THF over a period of 10-15 minutes. The solution remains colorless until the chloride is consumed (a minute or so), and then the Ge-Ge bond is reduced to give a dark green solution of the lithium reagent. Stir two hours under argon, then add the mixture over a period of several minutes to a solution of 4.0 gm $\phi GeMe_2Cl$ in 5 cc THF. The green color disappears immediately. Several small chips of Li are added, and the color slowly changes to yellow, orange, brown and finally dark green (~1/2 hour), this endpoint assuring total conversion of the chloride to the digermane. The solution is decanted from the lithium (color disappears upon contact with air) and evaporated. The residue is put into hexane, washed twice with water, then with NaCl, and dried over Na_2SO_4 and stripped.

Upon distillation, some solid plugged up the condenser (the product melts at 25.5 - 26.5° C[1]), The product bp~147°, ~.8 mm) appeared to be

cloudy and contaminated, but was pure enough by vpc and nmr, so was not redistilled. Yield 4.25 gm (63.5%).

The synthesis was repeated using 25 cm. Li ribbon and 5 gm portions of the chlorogermane, the reaction continuing for 1-1/2 hours. The crude yield (before distilling) was 8.20 gm. Solid again formed in the condenser, but it appeared to sublime. The apparatus was taken apart and cleaned, and the product distilled at 138 - 143° (.8 - .9 mm). All fractions were identical to the previous sample by vpc and nmr. Yield 6.4 gm (76.5%).

Synthesis of $\emptyset(GeMe_2)_2$ Cl by Hydrochlorodephenylation of $\emptyset(GeMe_2)_2\emptyset$.

Work in the literature[1] indicates only a 41% yield in this synthesis if anhydrous HCl is bubbled through a solution of the digermane in $CHCl_3$ with $AlCl_3$ as a catalyst. The rest of the material might well have gone all the way to the dichloride, so another system or technique was indicated.

.1 gm $\emptyset(GeMe_2)_2\emptyset$ was placed in 3 cc $CHCl_3$ with ~50 mg $FeBr_3$. HCl was bubbled through, and the reaction was to be followed by vpc. All the starting material was gone after only a couple of minutes, with the sole product having a short retention time (later shown to be the dichloride).

The reaction was repeated using .1 gm of the digermane in 5 cc CCl_4 with $FeBr_3$ (which is almost insoluble in CCl_4). 5 cc HCl was added with a gastight (greased) syringe, and with stirring was immediately taken up to give an orange-brown solution. After a few minutes some monochloride was evident. 10 cc more HCl was added in increments, and after 1/2 hour all the starting material was gone and the monochloride peak reached a maximum. Twenty minutes later, another peak (the dichloride) began to

grow. 10 cc more HCl was added, and after 20 minutes more all of the monochloride had gone to the dichloride.

This was repeated again in CCl_4 with $FeBr_3$, and it was again found that as the HCl was added in increments, the starting material peak on the gas chromatograph decreased as the monochloride increased. The starting material was completely used up and the monochloride reached a maximum before any of the dichloride formed, and upon further addition of HCl the monochloride disappeared as the dichloride reached a maximum.

It was also found that the peak due to the impurity initially present grew somewhat. The solvents were checked by vpc and found to be pure.

The approximate relative retention times at 175° C and 75-80 cc/min of helium on the Se-30 column are:

solvent	5 - 6
Cl $(GeMe_2)_2Cl$	8
unknown impurity	10
$\phi(GeMe_2)_2Cl$	21
$\phi(GeMe_2)_2\phi$	60

.25 gm (.695 millimole) $\phi(GeMe_2)_2\phi$ was placed in 5 cc CCl_4 with $FeBr_3$. This should require 15.6 cc HCl (at STP) to go completely to the monochloride. 5 cc HCl was injected. The solution darkened and some fluffy brown-black solid formed. 5 cc more HCl was injected. As the reaction progressed, the "impurity" peak got larger. This impurity, from the original ϕ_2GeMe_2 synthesis, was apparently being formed in the reaction. [Note: In later attempts at this reaction, this problem did not arise]. After 15.6 cc HCl and 50 minutes, the starting material was almost gone and none of the dichloride was present. The reaction was complete after another 30 minutes.

The reaction was repeated using THF as a solvent instead of CCl_4. The catalyst is very soluble in THF. An equivalent of HCl was added, but there was no appreciable reaction after 2 hours, and only 10% after 24 hours. More catalyst was added, along with 5 cc more HCl. The impurity peak got much larger and the reaction went about 75% of the way in a few minutes. More HCl and more catalyst were needed to complete the reaction, indicating possible poisoning of the catalyst (the brown-black solid may be the catalyst coming out of solution). No dichloride was formed.

The last two reaction mixtures were filtered and stripped, and then distilled (bulb-to-bulb) at 100 - 110°C (2 - 3 mm) to give a yellow liquid which solidified when cooled with acetone. The literature boiling point is 149° at 24 mm.[1] The nmr spectrum indicated impurities, and the vpc showed 9 compounds present, with 4 in major quantity. This might be due to moisture or from having distilled off of the $FeBr_3$ which remained, or from having sat over the catalyst too long (several days) before distilling.

.25 gm $\emptyset(GeMe_2)_2\emptyset$ was left overnight in CCl_4 with $FeBr_3$. Vpc indicated some monochloride formed, and the impurity peak became quite large. The starting material disappeared completely with the addition of 10 cc (2/3 equivalent) of HCl.

.10 gm $\emptyset(GeMe_2)_2\emptyset$ was placed in 5 cc $CHCl_3$ with a lot of $AlCl_3$ catalyst, this being the system used by Kumada et. al.[1] Too much aluminum chloride was added, as the reaction went completely to the dichloride without any HCl being added.

.05 gm $\emptyset(GeMe_2)_2\emptyset$ was placed in 2 cc $CHCl_3$ and a few milligrams $AlCl_3$ was added. A small amount of monochloride formed immediately.

HCl was added in small increments by syringe, but the reaction was slow and evidently required more catalyst. After 1-1/4 hours and several equivalents of HCl, the starting material disappeared and the monochloride was at a maximum with no dichloride present. After more time and more HCl, the dichloride was seen to form. The system was purged with nitrogen, and the next day both products were still present as the only major components.

The reaction was repeated using .10 gm $\emptyset(GeMe_2)_2\emptyset$ in $CHCl_3$ with $AlCl_3$ catalyst. Addition of HCl converted the starting digermane selectively and quantitatively to the monochloride. After three days sitting over the catalyst, only a trace of the dichloride had formed. 1 cc of acetone was added to deactivite the catalyst,[1,4] and the product was distilled bulb-to-bulb. Vpc showed several components, the desired product being better than 95% pure, with one impurity at several percent and two others at less than one percent. The nmr spectrum was fairly clear. A microanalysis has not yet been done.

Synthesis of Diphenyltetramethyldigermoxane

15 drops of an impure fraction of $\emptyset GeMe_2Cl$ were placed in 3 cc H_2O with Na_2CO_3. Much solid formed in the violent reaction. The solution was extracted twice with 2 cc ether, and the ether was washed with saturated NaCl and dried over Na_2SO_4. Vpc indicated no germanium compounds present in the solution.

Following a procedure used earlier by Manning Cooke, .2 gm of the above impure $\emptyset GeMe_2Cl$ was dissolved in 12 cc ether with Na_2CO_3 present. 5 cc H_2O was added, and the mixture was stirred one hour and then

dried over Na_2SO_4. The ether was evaporated to yield the crude product consisting of approximately 60% of the digermoxane (presumably) and 40% of the impurity originally present (and also desired for isolation). The retention times are sufficiently different for preparative gas chromatography.

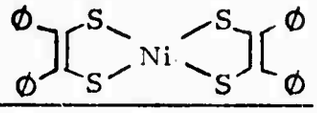
TABLE I

Physical Constants and Proton NMR Data for Organogermanes[a, b]

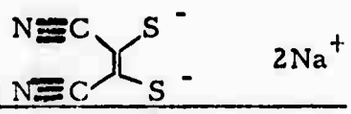
Compound	Mol. Wt.	B.p. (°C/mm)	Best Yield(%)	Earlier Reported Yield [c]	Chemical Shifts(c.p.s.) Me	Ø
$Ø_2GeMe_2$	256.86	123-128/1	79.0	81	38	432-456
$ØGeMe_2Cl$	215.20	116-124/16	85.3	86	56	436-460
$Ø(GeMe_2)_2Ø$	359.51	138-143/0.8-0.9	76.5	93	29	432-440
$Ø(GeMe_2)_2Cl$	317.87	--	--	41	39($ØMe_2Ge$-) 43($ClMe_2Ge$-)	432-448

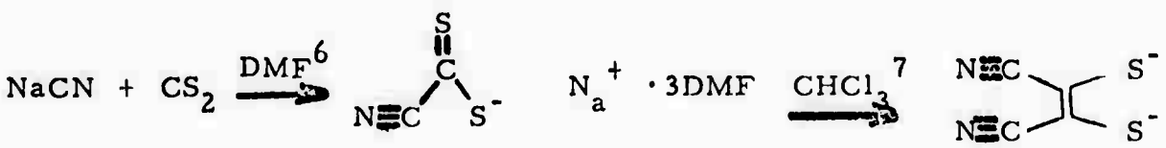
[a]No microanalyses were done on these preliminary compounds. [b]Mass spectra will be done in the near future. [c]Kumada et. al. J. Organomet. Chem., 17, 235 (1969).

Miscellaneous Experiments

Preparation of Bis(dithiobenzil) nickel, 

10 gm (.0472 mole) benzoin was refluxed with 20 gm P_2S_5 in 70 ml dioxane for 5 hours. The mixture was then cooled and filtered, the filtrate being dark brown and the residue white. To the filtrate was added 5 gm $NiCl_2 \cdot 6H_2O$ in 20 cc H_2O, and this was heated on a steam bath for three hours and then cooled. The green-black crystals were collected by filtration and washed in 50% dioxane in acetone and then several times with pure acetone. First crop yield 2.50 gms. The concentrated filtrate yielded an additional .25 gms. mp 272° (uncorrected). Reported mp 292° dec.[5] Yield 2.75 gm (21.5%).

Preparation of 



9.8 gm dry, finely pulverized NaCN and 60 cc DMF are placed in a 3-neck flask with a mechanical stirrer and a reflux condenser with a drying tube. The mixture is cooled to 0° and, while stirring, 15.2 gm (12.0 cc, .20 mole) CS_2 is added over a period of 10 minutes. Stir 30 minutes at room temperature. The brown mass formed is diluted

to 200 cc with isobutanol and warmed until all is dissolved, after which time the warm solution is filtered to remove excess NaCN (a heatlamp is needed to keep the mixture liquefied). The sodium salt of the DMF complex crystallizes out of the cooled filtrate, and is filtered and washed with small amounts of isobutanol and then with ether. No recrystallization was necessary. Air dry to remove ether (product reacts slightly with air). Yield 55 gm (80%).

The prepare the dianion, 34.5 gms (.10 mole) of the above prepared anion is dissolved in 110 cc $CHCl_3$ and the solution is filtered. The filtrate is allowed to set four days at room temperature (under nitrogen), and is then filtered, and the residue is washed with $CHCl_3$ and Et_2O to remove elemental sulfur. The residue is then taken up in methanol (as little as possible), filtered, and the filtrate concentrated slightly and cooled to -20°C, adding a little ether to induce crystallization of the pale yellow product.

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4. Although $AlCl_3$ will complex with acetone, it seems unlikely to me that this complex would not decompose during the subsequent distillation, leaving behind the $AlCl_3$.

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STUDIES ON TIN-TIN BONDED SYSTEMS

Norvell Nelson

Tin-Tin Bonds

Following the development of a theory of high-temperature superconductivity by Professor W. A. Little, an effort is being made to synthesize model compounds that could be used for experimental verifications of the theory. Of the many possible approaches to the synthetic problem the catenated chains of the Group IVa elements appear to offer, in the long run, the best possibility of achieving a practical model for a synthetic superconductor.

All of the Group IVa elements, save lead, are capable of catenation. Carbon , the first member of the group, is well known for its catenation, however, the theory requires that the metal backbone (the catenated Group IV element possesses a fairly low lying conductor band. A saturated carbon chain would not have this property since a long chain of unsaturated carbons would not conjugate, but would be more like a series of ethylenes. The remaining Group IV elements, silicon, germanium and tin, upon catenation could have a suitable conduction band formed by overlap of the "d" orbitals. However these "d" orbitals are normally vacant, so some means of populating this band would be necessary. One possible solution would involve the appending of suitable transition-metal complexes on the backbone with the idea that the metals would act as electron donors.[1]

As outlined in reference 1a each of the three Group IV elements (Si, Ge or Sn) has several drawbacks as far as its workability in synthetic schemes for catenation. In spite of published compilations of homonuclear bonds strengths (Si >Ge >>Sn)(with an Sn-Sn bond said to be worth ~ 35 kcal) they have almost comparable bond strengths.[2b] The Si and Ge homo(and mixed)-nuclear bonds are air and water stable; the intermediate monomers, however, are exceedingly water sensitive and interaction with water leads to M-O-M species. Happily, they are non-toxic. Unfortunately, they do suffer from the non-existence of a good, specific metal-metal coupling reaction - a definite impediment to catenation.

Tin, on the other hand, possesses a general homonuclear bond forming reaction of apparently general utility.[1a] Tin also forms much stronger bonds to transition-metals than either germanium or silicon. However, tin-tin bonds are extremely air-sensitive; some tin catenates are pyrophoric.[3] The organotin intermediates usually are both oxygen and water sensitive in addition to their toxicity, acute for some compounds.[4] These problems notwithstanding, it was thought that generation of a catenated tin chain would be extremely useful since the gap between the bound electrons and the overlapped "d" orbitals - the conduction band - would be small.

Some careful work on tin catenates was done by Brown[5] and Neumann.[6] Brown characterized the various products obtained from the reaction of dimethyltin dichloride with sodium in liquid ammonia (reaction 1). This

$$Me_2SnCl_2 + Na(xs) \xrightarrow{NH_3} (Me_2Sn)_n \qquad 1$$

reaction was not reliable for different products were obtained under supposedly identical conditions. In one case, a cyclic product was obtained having n=6. At other times, linear (or thought to be so) species were obtained having n=12 to 20; one preparation gave a product having an estimated n=70. All of these compounds, save the cyclic hexamer, were yellow air-sensitive oils or semi-solids that were difficult to purify. Neumann characterized some of the polytins obtained from the catalytic dehydrogenation of diorganotin hydrides. The best catalysts are organic amines with

$$R_2SnH_2 + \text{catalyst} \longrightarrow (R_2Sn)_n + H_2 \qquad 2$$

dialkyl amines, or better yet, dialkyl amine adducts of the corresponding diorganotin dichloride being the most active catalysts. For R=phenyl, n was found to be 6 - while for R=ethyl, n=9. Both materials were cyclic. These polytins were yellow, air-sensitive solids. The polytins obtained from other organotin dihydrides were also cyclic materials with the value of n dependent on the organo group.

The work of Brown and Neumann demonstrates that tin catenates are stable isolable species that persist in absence of air. These compounds have limited utility in the present study owing to their cyclic nature. Since the desired model compounds are linear chains of definite composition, it appears from the above work that uncontrolled polymerization of tin monomers would not be a fruitful approach. However, controlled cleavage of some of the cyclic materials to give difunctionalized organotin chains is. There is one report in the literature of a direct synthesis of terminally functionalized organotin chains. Unfortunately, this work was not

$$R_2SnCl_2 + Na \xrightarrow[\text{reflux}]{\text{xylene}} Cl[R_2Sn]Cl$$

for R=Methyl n=2
R=Ethyl n=4
R=n-Propyl n=3
R=n-butyl n=5

reproducible. Owing to the high melting points reported for these catenated chlorides there is a strong suspicion that they are, in fact, hydrated oxides or a hydroxy halo species.*

From the brief outline above, we see that in principle a chain of catenated tin atoms can be synthesized and once made is intrinsically stable in the absence of air. However, considering the difficulties surrounding the preparation of discrete tin chains by direct polymerization of a monomer, stepwise synthetic schemes for elaboration of the chain are required.

Following the noteworthy success of M. Cooke and Japanese workers on the germanium problem using the intermediacy of dimethylphenylgermanium chloride. With germanium this chloride is readily obtainable from dimethyl-

$$\phi Me_2GeCl \xrightarrow{Li} \phi Me_2GeLi \xrightarrow{\phi Me_2GeCl} \phi Me_2GeGeMe_2\phi$$

$$\phi Me_2GeGeMe_2\phi \xrightarrow[\text{Lewis Acid}]{HCl} \phi Me_2GeGeMe_2Cl \xrightarrow[\text{coupling}]{\text{repeat}}$$

*For R=Et, these workers[7] report that their product $Cl[Et_2Sn]_4Cl$ has a m.p. 179-182°, while Coates[3] (p. 446) notes that diethyltin dichloride and diethyltin oxide form $(ClEt_2Sn)_2O$ m.p. 176°.

diphenylgermanium by cleavage (cleanly) of one phenyl group with HCl in a Lewis acid catalyzed reaction. Unfortunately, the procedures used to synthesize dimethylphenylgermanium chloride fail miserably for tin.

In fact, the preparation of the dimethylphenyltin chloride proved to be a major problem. Using the germanium procedure, one obtained exclusively dimethyltin dichloride even when the Lewis acid catalyst was omitted. The compound is cleanly prepared from dimethyldiphenyltin and mercury(II) chloride.* This chloride should be used immediately upon preparation

$$\phi_2Me_2Sn + HgCl_2 \longrightarrow \phi Me_2SnCl + \phi HgCl$$

owing to its tendency to disproportionate upon standing. This chloride was

$$2\,\phi Me_2SnCl \longrightarrow \phi_2Me_2Sn + Me_2SnCl_2$$

not used in reactions paralleling those of the germanium series, since the dimer produced would again have to be cleaved to give functionalized material

$$\phi Me_2SnCl \longrightarrow \longrightarrow \phi Me_2SnSnMe_2\phi \xrightarrow{\text{cleave}}$$

to continue the process. An attempted cleavage of hexamethylditin with mercury(II) chloride failed.** Another weak point in this approach using tin

$$Me_3SnSnMe_3 \xrightarrow{HgCl_2} Me_3SnSnMe_2Cl$$

$$Me_3SnSnMe_3 \longrightarrow Hg + 2Me_3SnCl\ ^{\ddagger}$$

anions is the facile degradation of polytins by these anions.

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*The dimethyldiphenyltin does not yield the chloride upon treatment with HCl (uncatalyzed and cold), $SiCl_4$, $TiCl_4$, $SnCl_4$ or NBS under the conditions tried.

**Both trimethyltin chloride and dimethyltin dichloride can be prepared from tetramethyltin by varying the Sn/Hg ratio from 1:1 to 1:2 (see Experimental).

‡It appears that this reaction should not have been unexpected since $Et_3SnSnEt_3 + \phi_2Hg \longrightarrow 2Et_3Sn\phi + Hg$ occurrs with the much weaker electrophile ϕ_2Hg?

In a very elegant dissertation Creemers[2a] developed a series of tin-tin bond forming reactions of, it appears, general utility. The general reaction involves a tin hydride and a tin amine or other tin nitrogen

$$Me_3SnH + \phi_3Sn\text{-}NMe_2 \longrightarrow \phi_3SnSnMe_3 + HNMe_2$$

compounds. With a suitable modification a ditin hydride can be obtained. The beautiful part of this preparation concerns the ready availability and

$$Et_2SnH_2 \longrightarrow Et_3Sn\text{-}N(CHO)(\phi) \longrightarrow Et_3SnSnEt_2H + \phi N(H)CHO$$

high reactivity of the tin-amido compound. Activated tin compounds of this type are obtained by direct reaction of a tin hydride and phenyl isocyanate.

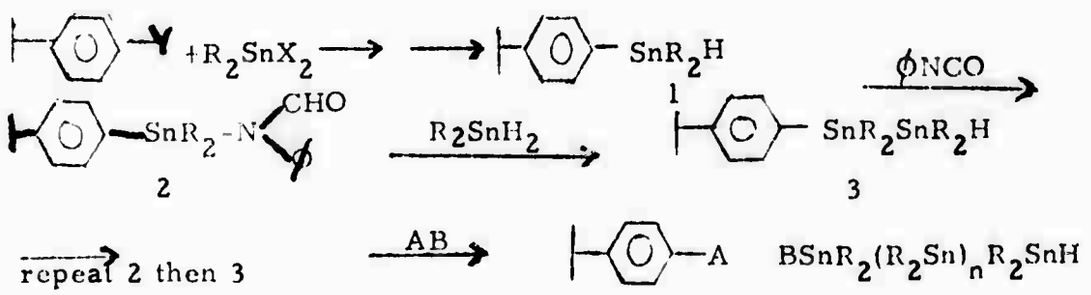
$$Et_3SnH + \phi NCO \longrightarrow Et_3Sn\text{-}N(CHO)(\phi)$$

As outlined in reference 1a the above series of reactions immediately suggest a cyclic process for building a tin chain. This type of cyclic

$$R_3SnH + \phi NCO \longrightarrow R_3Sn\text{-}N(CHO)(\phi) \xrightarrow{R_2SnH_2}$$

$$R_3SnSnR_2H + \phi N(H)CHO \xrightarrow{\phi NCO} R_3SnSnR_2\text{-}N(CHO)(\phi) \xrightarrow{R_2SnH_2} \text{and repeat}$$

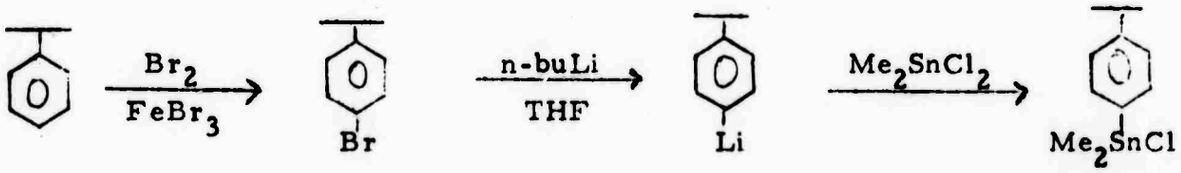
process is also reminiscent of peptide synthesis and the polymer support method developed by Merrifield.[9] The main advantage of the "Merrifield" method is in the work-up; a simple filtration being all that is required. Application of this method to the tin problem requires the following sequence: 1) attachment to the polymer; 2) activation of the bound tin; 3) extension of tin



chain by a unit (repeat of 2 and 3 until desired length achieved); 4) cleavage of discrete tin chain from the polymer support.

Steps 1 and 4 are the most critical in the scheme and are intimately coupled to each other since both involve the tin polymer bond. Ideally, this bond will be inert to the reaction conditions (steps 2 and 3), but will be sufficiently labile so that it will be cleaved in preference to other bonds in the chain.

Owing to the fact that tin-phenyl bonds are cleaved by electrophiles much faster than tin-alkyl bonds,[10] it was thought that the tin could be bound directly to the phenyl ring of the polymer. The tin chloro compound

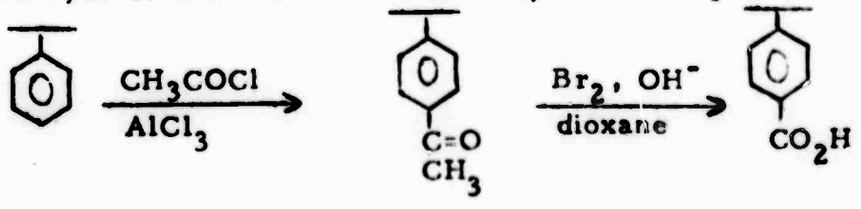


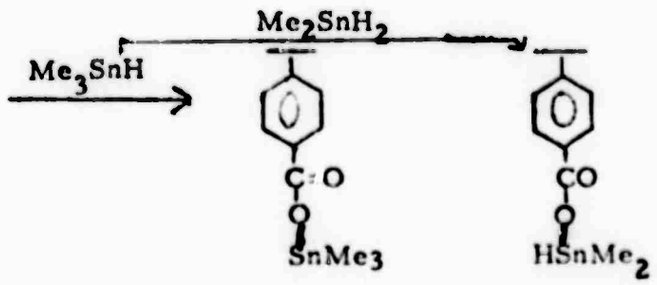
on the polymer is then readily extended via the hydride-isocyanate sequence. However, cleavage by an electrophile (acetic acid) would have to react much faster with the tin-phenyl bond than with the many tin-alkyl bonds on the chain, a not too likely situation since the rate difference is not all that large. (The tin-tin bond is stable to acetic acid, while this reagent will readily cleave

$$Ph_3SnSnPh_3 + HOAc \xrightarrow[120^\circ]{} Sn_2OAc_6$$

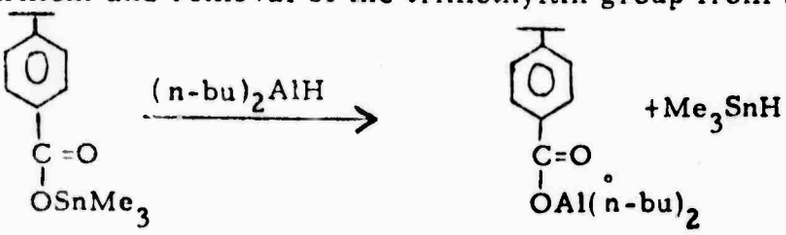
tin-phenyl bonds.[11])

An alternate mode of attachment to the polymer utilizes a tin ester linkage. A tin hydride will react with a carboxylic acid to give a tin ester, a linkage



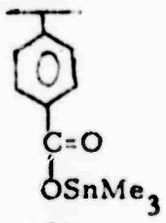


that should be stable to a tin hydride. Again, attachment to the polymer insures isolation of a reactive species.* Cleavage from the polymer is readily affected, in this case with diisobutylaluminum hydride. The attachment and removal of the trimethyltin group from the polymer has

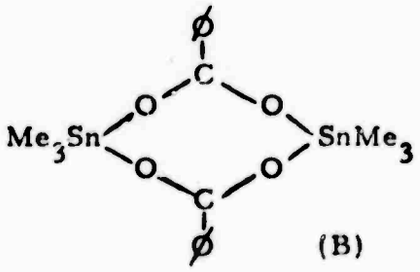


been accomplished according to the steps outlined above.

An interesting sidelight to the reaction of trimethyltin hydride with the carboxylic acid resin illustrates the utility of the polymer support for isolation of reactive species. The trimethyltin group bound to the polymer (A) looks like a normal benzoate in the infrared, ν_{CO} at 1720 cm^{-1}.



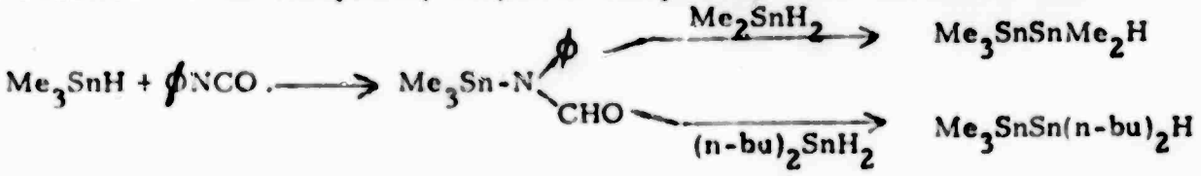
(A)



(B)

Trimethyltin benzoate is a dimer (B) and the carbonyl frequencies are much lower with ν_{CO} at 1590 and 1550 cm^{-1}.

As a test and a model for the polymer reaction with the tin dihydride the reaction was attempted without the polymer support. Creemers[2a] describes the reaction for the completely ethylated compounds. For the mixed case



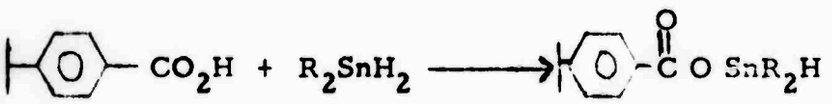
*Reaction of a dialkyltin dihydride and a dialkyltin dicarboxylate yield the dialkyltin hydrocarboxylate, but in solution at 20°

$(n\text{-bu})_2SnH_2 + (n\text{-bu})_2Sn(OAc)_2 \longrightarrow 2(n\text{-bu})_2Sn(H)OAc \xrightarrow{20°} [(n\text{-bu})_2SnOAc]_2$

the hydrocarboxylate reacts with itself giving the ditin.[12]

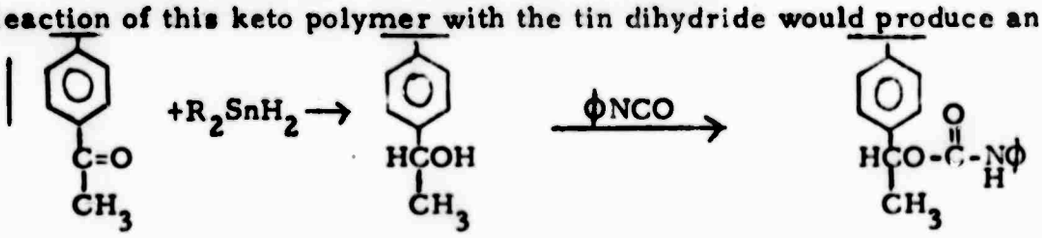
(methyl and n-butyl) attempted, trimethyltin hydride was allowed to react with phenyl isocyanate giving the tin amido compound (above). Following the reaction of this intermediate with di-n-butyltin dihydride, a clear liquid was obtained. It had a very strong Sn-H absorption in the infrared (1780 cm^{-1}), but was found to be a mixture by nmr. Compounds of this type were neither successfully distilled nor run through the glc without some decomposition.

A parallel synthesis of a tin-tin bond was attempted on the polymer. In most cases, the first step with a tin dihydride did not yield a resin with a strong



CO absorption in the IR. Reaction of this polymer with phenyl isocyanate gave a product that once more had a CO absorption in the IR at 1710 cm^{-1}. Subsequent reaction with trimethyltin hydride yielded a polymer having only a weak CO absorption at 1720 cm^{-1}. Treatment with di-iso-butyl-aluminum hydride and analysis of the reaction by glc did not show the presence of anything attributable to the ditin hydride.

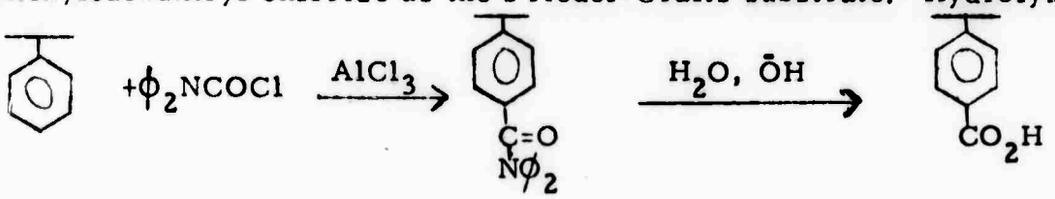
Since amplitude variations in the OH region matched those in the CO region, a non-productive series of reactions is also possible. Recalling that the carboxylic acid group was introduced by a difficult oxidation of a methyl ketone, it is quite possible that methyl ketone remained on the polymer. Reaction of this keto polymer with the tin dihydride would produce an alcohol



function accounting for the OH in the IR. Subsequent reaction with phenyl-isocyanate would yield an urethane having both NH(~OH) and CO absorptions. Further reaction with trimethyltin hydride is also possible.

Although the prospects of generating a tin catenate seem somewhat dim at the moment, the project should not be totally abandoned. After all, tin is the only Group IV element that has a workable homonuclear bond forming reaction. A slight modification of the above procedure may be more fruitful.

A more direct way into the carboxylic acid resin would utilize N, N-diphenylcarbamoyl chloride as the Friedel-Crafts substrate. Hydrolysis



would then give the carboxylic acid. Reaction of this resin with a ditin dihydride[12] might then give the functionalized resin required for tin chain

$$R_2SnH_2 + R_2SnOAc_2 \longrightarrow [R_2Sn\ OAc] \xrightarrow{LAH} [R_2SnH]_2$$

extension free from the complications due to the monotin dihydride.

In the long-run, success may be best achieved with a hybrid system. Given the ability of making sub-chains of Ge or Si, these may then be capped

$$X[R_2Ge]_n^X \xrightarrow{R_2SnX_2} X\ R_2Sn[R_2Ge]_nSnR_2X \xrightarrow[\text{coupling}]{\text{tin}} \text{polymer}$$

with functionalized tins and with the tin-tin coupling reaction go directly to the polymer.

Tin-Iron Compounds

The theory for the use of Group IV catenates as the "conducting" spine for the higher temperature superconductors concerns the energy gap between the bound electrons and the conduction band.[1] If this gap is too large in the pure Group IV catenates, several proposals have been made concerning ways of artificially lowering this gap.[1b] One proposal requires the attachment of low-valent transition-metal complexes to the Group IV catenates with the idea that they would act as electron donors. In pursuit of this idea several tin-iron compounds were investigated.

Owing to some interesting reactions of tin(II) chloride with organo-transition-metal compounds, several iron-tin compounds are readily available as

$$[cpFe(CO)_2]_2 + SnCl_2 \xrightarrow[heat]{MeOH} cpFe(CO)_2\text{-}SnCl_2\text{-}(CO)_2Fecp \quad [13]$$

(C)

$$[cpFe(CO)_2]_2 \xrightarrow{HCl,\ O_2} 2\ cpFe(CO)_2Cl$$

$$2\ cpFe(CO)_2Cl + SnCl_2 \xrightarrow{MeOH} cpFe(CO)_2SnCl_3 \quad [14]$$

(D)

intermediates. The diiron compound, C , can be alkylated the same as any other disubstituted tin dichloride.

$$[cpFe(CO)_2]_2SnCl_2 + 2MeMgX \longrightarrow [cpFe(CO)_2]_2SnMe_2$$

Since this reaction works, possibly a variation on the tin hydride coupling

$$[cpFe(CO)_2]SnCl_2 + 2\ LiNMe_2 \longrightarrow [cpFe(CO)_2]_2Sn(NMe_2)_2 \xrightarrow{Me_3SnH} [cpFe(CO)_2]_2Sn(SnMe_3)_2$$

reaction would also meet with success. The above reaction, in fact, did go as written, but in extremely poor yield. The second step liberates dimethylamine

which is an extremely effective catalyst for decomposition of tin hydrides. The tritin-diiron compound had both infrared (ν_{CO} 1956s and 1985 vs-benzene-d_6) and nmr data (2 singlets, one typical of cp δ=4.6 and Sn-Me at δ=0.6) consistent with the assigned structure. This reaction failed when dimethyltin dihydride was substituted for the trimethyltin hydride. Again, owing to the lack of suitable degradation reactions, the diiron polytin compound is of marginal utility even if the yield were improved.

A variation of the above reaction was attempted by first conversion of $[cpFe(CO)_2]_2SnCl_2$ to the dihydride and $[cpFe(CO)_2]_2SnCl_2$ -

$$\xrightarrow{LiAlH_4} [cpFe(CO)_2]_2SnH_2 \xrightarrow{\phi NCO} [cpFe(CO)_2]_2Sn(N\langle_{\phi}^{CHO})_2$$

and subsequent conversion of the dihydride to the tin bis-amido compound with phenyl isocyanate. It appears that the first step does occur; if $[cpFe(CO)_2]_2SnCl_2$ is treated with a stoichiometric amount of lithium aluminum hydride in THF/ether at -78° a white solid separates, probably $LiAlCl_4$, while the solution maintains its color. Slight warming of this solution results in the immediate evolution of a gas accompanied by a darkening of the solution. After sitting at room temperature the solution deposits some black insoluble material. This material is pyrophoric, but still possesses both C_5H_5 groups and coordinated CO. It is probably a high polymer containing tin-tin bonds.

The same reaction was attempted with $cpFe(CO)_2SnCl_3$.

$$cpFe(CO)_2SnCl_3 \xrightarrow[LiAlH_4]{} \{cpFe(CO)_2SnH_3\} \longrightarrow \text{black, insoluble material}$$

Again the same results obtained as with $[cpFe(CO)_2]_2SnCl_2$; a black, insoluble pyrophoric material was isolated. This material still had both cp and CO groups (by infrared).

An important step in the characterization of these pyrophoric materials would be the determination of the tin iron ratio. To this end several weeks were expended in devising a suitable analytical scheme for this determination.

Unfortunately, both Fe(III) and Sn(IV) behave quite similiarly in EDTA titrations, for example, both are masked (and demasked) by the same reagents. Several schemes were devised but none had sufficient reproducibility or standard solutions to be reliable for the unknowns. With the rumors rampant about the impending arrival of an atomic absorption spectrometer, efforts in this direction were discontinued. If interest revives in the wet methods, a potentially useful scheme is outlined below.

Proposed Analytical Scheme for Tin and Iron

The indirect EDTA titration method of Kinnunen and Wennerstrand[15] should, in principle, work for the simultaneous determination of tin and iron. Indirect EDTA methods, in general, are required for iron since the aqueous iron usually forms stronger complexes with the indicator dye than it does with EDTA. In the above method, T hIV is the best back titrant for low pH systems. However, the recommended procedure[16] for digestion of organotin compounds requires fuming down with sulfuric acid. Unfortunately, sulfate ion interferes with the ThIV-EDTA reaction.

Slight modifications of some literature procedures whould enable one to affect the required metal analyses. Digestion of the sample[16] will yield aqueous solutions of Fe(III) and Sn(IV). The iron may then be determined titrimetrically using CeIV, with Sn(II) used as the reducing agent in the standard way.[17] Following the determination of iron, the total (iron and tin) can be determined on another portion using the same titrant with sodium diphenylamine sulfonate as indicator. Both species can be reduced by bailing with nickel shot.[18] This reductant can readily be removed just before titration with the aid of a magnetic stirring bar retriever. The Fe(II) and Sn(II) are then readily titrated with Ce(IV).

Experimental

Preparation of Tetraorganotins and Organotin Halides

Tetramethyltin:

Tetramethyltin was prepared using the approach of Edgell and Ward.[19] Methyl Grignard was made by bubbling methyl chloride through a suspension of 50g (2.06 moles) of magnesium turnings in n-butyl ether until most of the metal disappeared (about 6 hrs.). Next, $SnCl_4$ (75g, .29 mole) was slowly added to the Grignard solution maintaining solvent reflux. After stirring overnight the product was distilled directly from the reaction mixture. A second distillation yielded 24 g (47%) of tetramethyltin, b.p. 73-76°.

Dimethyltin Dichloride:

Dimethyltin dichloride was prepared by allowing tetramethyltin to react with 2 mole of mercury(II) chloride.[20] Tetramethyltin 3g (.017 mole) was added to 9g (.033 mole) of mercury(II) chloride in 50cc absolute alcohol at room temperature. Immediately upon addition a white precipitate formed. After cooling, the white solid was separated by filtration giving 8.3g (essentially 100%) of methyl mercury chloride. Evaporation of the ethanol and crystallization from ethyl acetate - hexane yielded 2.7g (72%) of dimethyltin dichloride.

Trimethyltin Chloride:

With the mercury(II) chloride tetramethyltin ratio set to 1:1, trimethyltin chloride can be obtained as the product. 6g (.033 mole) of the tetramethyltin by the above procedure yielded 6.7 g (99%) of trimethyltin chloride.

Dimethyldiphenyltin:

Dimethyldiphenyltin was prepared by the reaction of methyl Grignard and diphenyltin dichloride, or by reaction of phenyl Grignard and dimethyltin dichloride. The first procedure will be given in detail. A solution of methyl Grignard was prepared in ether by slowly bubbling methyl chloride into a stirred suspension of magnesium (12g) until most of the metal disappeared. After settling the clear super was transferred by syringe to a solution of 32g (.09 moles) of diphenyltin dichloride (Mand T Chemicals) in 100 cc of ether. After stirring for one-half hour, the reaction mixture was filtered

and the ether was evaporated. The resulting colorless liquid was vacuum distilled, the fraction boiling 103-106°/~.5 mm was retained; yielding 24.9g (88%) of a colorless liquid. The compound was essentially pure by glc analysis (SE-30, ~200°). The nmr spectrum consists of a complex multiplet centered at 7.3δ (phenyl) and a sharp singlet at .45δ (methyl) flasked by a pair of satellites due to coupling to 117 Sn and 119 Sn. Integrated ratio (phenyl to methyl) was 1 3/4:1, theory 1 2/3 to 1. Analysis: Theory C 55.83, H 5.32; Found, C 55.19, H 5.33.

Dimethylphenyltin Chloride:

It was found that dimethyldiphenyltin could be cleaved selectively with mercury(II) chloride using a procedure similar to that previously employed. A mixture of 15g (.049 mole) of dimethyldiphenyltin and ca. 100cc absolute ethanol was cooled to -78°. The required 13.55g of mercury(II) chloride was dissolved in 75cc absolute ethanol and this solution was slowly added to the cold solution of the organotin. Initial addition resulted in the immediate precipitation of a white solid. After all the mercury(II) chloride was added the reaction mixture was filtered giving 14.95g of white solid (phenylmercury chloride, 97%) and a clear solution. The ethanol was evaporated and the residue dissolved in ether and extracted 3x with water (to remove any dimethyltin dichloride). Evaporation of the ether yielded a colorless liquid, pure by glc. This material was subjected to vacuum distillation, the fraction boiling 95-98° at 4.4mm was retained as the purest (by glc). (It is important to note that glc disclosed the presence of both dimethyltin dichloride and dimethyldiphenyltin in the distilled material while these materials were absent prior to distillation.) Pmr spectrum consists of a multiplet centered at 7.5 and a singlet at 0.8 (having 2 pair of satellites, $J^{117}Sn \sim 56Hz$ and $J^{115}Sn^{119} \sim 60Hz$) with an integrated ratio of phenyl to methyl of .84 to 1 (theory .83 to 1). Analysis: Theory; C, 36.77; H, 4.24; Cl, 15.08; Found: C, 35.04; H, 4.14; Cl, 14.73.

Preparation of Tin Hydrides

Di-n-butyltin dihydride[21]

To a well-stirred solution of 10g (.26 mole) of lithium aluminum hydride in 200 cc ether, a solution of 100g (.36 mole) of di-n-butyltin dichloride

(K and K Chemicals) in 300 cc ether was slowly added at a rate that maintained the refluxing of the ether. After complete addition of the tin chloride, the solution was refluxed an additional 2 hours. The excess lithium aluminum hydride was destroyed by slow addition of wet glyme. The resulting mess was filtered and the solvent evaporated. The liquid residue (79g) was distilled at reduced pressures. The fraction boiling at 63°/4.5 mm was retained, 43.4g (55%). The infrared spectrum showed a very strong νSn-H at 1835 cm^{-1}. The pmr spectrum consisted of a quintet at 4.8δ (Sn-H) flanked by 2 pair of satellites (about 1000 Hz at either side due to ^{117}Sn and ^{119}Sn) and a complex multiplet from 0.8 to 1.8δ (n-butyl). Integrated ratios for Sn-H to n-butyl are: Calc., 1:9; Found, 1:-10.

Tri-n-butyltin Hydride[22]:

This tin hydride was using the same procedure for di-n-butyltin hydride. 63g of tri-n-butyltin chloride yielded 49.5g of vacuum distilled hydride (92%). The pmr spectrum consisted of a septet at 5δ flasked by ^{117}Sn and ^{119}Sn satellites about 1000 Hz on both sides and a complex butyl forest from 0.2 to 2.2δ. The infrared spectrum had a νSnH at 1805 cm^{-1}(s).

Dimethyltin Dihydride and Trimethyltin Hydride:

Several methods, including a published procedure,[23] were used to prepare this low-boiling (33°) hydride. The last proceudre used yielded the cleanest product. Owing to the low boiling point of the hydride a high-boiling solvent was employed, the most conveninet being tetraglyme. The dimethyltin dichloride 45g (.205 mole) in 100 cc tetraglyme was added slowly to an excess of lithium aluminum hydride in 200 cc tetraglyme. After the addition was complete the reaction mixture was stirred for an additional 2 hours. The volatile hydride was then removed simply by pumping out the reaction mixture through a liquid nitrogen trap. This preparation yielded 29g of the hydride (97%). The pmr spectrum consists of a septet (at ~ 4.60) flasked by the ^{117}Sn and ^{119}Sn satellites and a triplet about 0.δ. Trimethyltin hydride is also prepared using this procedure.

Preparation of Polystyrene and Substituted Polystyrenes

"Popcorn" Polystyrenes:

Several batches of "popcorn" polystyrene were synthesized using the method of Letsinger.[24] In addition several functionalized "popcorn" polystyrenes were also prepared by co-polymerizing styrene with, for example, p-bromostyrene. The "popcorn" polymers from this process proved to be marginally useful owing to the simultaneous formations of a soluble polystyrene which could be separated from the "popcorn" polymer by repeated washings with boiling chlorobenzene. This procedure usually yielded "popcorn" polymer in only 5-10%.

Substituted Bio-Beads:

Substitution reactions on 2% cross-linked polystyrene ("Bio-Beads") were performed according to literature procedures.[24] The resin was brominated using Br_2 in acetic acid with added $FeBr_3$ as a catalyst. This procedure yielded a resin having 5.2% Br (about 6% of the rings were substituted).

The carboxylated resin was prepared from the "Bio-Beads" using Letsinger's[24] two-step procedure. The resin was first acetylated using acetyl chloride and aluminum chloride yielding a resin having a strong band at 1670 cm^{-1}. This keto resin was then treated with basic bromine to effect oxidation to the acid. Two repeated oxidations were required to give a resin with a diminished 1670 cm^{-1} band. The product from the second oxidation titrated for 1.2 meq acid per gram, but still had ν_{CO} at 1675 and a new band at 1685 cm^{-1}.

Reaction of Carboxylic Acid Resin with Trimethyltin Hydride:

1 gram of carboxylated resin, containing 0.36 meq. of acid, was suspended in 40 cc of butyronitrile containing 15 cc of trimethyltin hydride and stirred overnight. The resin was worked up by filtering and by washing four times with THF. Infrared spectrum had ν_{CO} at 1680 (s) and 1720 (m) cm^{-1}. Attachment of the Me_3Sn group to the resin was confirmed by cleavage to Me_3SnH with di-iso-butylaluminum hydride. After treatment of the tin resin with .2 cc of the aluminum hydride in 5 cc of benzene trimethyltin hydride was identified in the reaction mixture by glc.

Tin-Tin Bonds:

Procedure of Creemers[2] worked quite well for trimethyldibutylditin hydride. The product did not survive distillation and, as noted previously, was not pure as made.

Tin-Iron Compounds:

Preparation of $[cpFe(CO)_2]_2Sn(SnMe_3)$

4.7g (8.6 m mole) of $[cpFe(CO)_2]_2 SnCl_2$[13] was dissolved in 30 cc ether at -78°. While at this temperature a slurry of 2g (39 m mole) of lithium dimethylamide in ether was slowly added to the iron compound. The reaction mixture darkened to a red-brown. It was stirred at -78° for 3/4 hour and stored in freezer for 2 hours. After filtering 25 cc of heptane was added and the ether removed yielding a dark-red purple powder.

After attempted recrystallizations of this material still apparently yielded a mixture, the residues were treated with excess trimethyltin hydride in butyronitrile. The product came out of benzene heptane and had spectral properties consistent with the formulation $[cpFe(CO)_2]_2Sn(SnMe_3)_2$.

IR ν_{CO} at 1950 s, 1985 vs, 1780 w (due to $[cpFe(CO)_2]_2$) NMR - a mixture but two singlets one in cp region and one in $SnMe_3$ region.

Experiment definitely needs repeating.

$[cpFe(CO)_2]_2 SnCl_2$ and $cpFe(CO)_2SnCl_3$ with Lithium Aluminum Hydride

The procedures for both substrates are identical so only one will be described in detail. A standard solution of lithium aluminum hydride (LAH) was made in ether by dissolving commercial LAH in ether, filtering, and titrating an aliquot with standard acid.

2.5g (4.6 m mole) of $[cpFe(CO)_2]_2SnCl_2$ was dissolved in 70 cc of tetrahydrofuran (THF) at -78°. To this solution the requisite amount of LAH solution (4.1 cc of .55m LAH) was added at one time. This mixture was stirred at -78° for about 2 hours. (During this time in some of the preparations a white material, presumably $LiAlCl_4$, came out of solution.) After 2 hours, the solution (still pale yellow) was allowed to warm to room temperature. As the warming proceeded the solutions would darken to a dark red brown and finally to dard brown, all the while evolving a gas, probably H_2. Filtration

yielded a black powder which was pyrophoric. Slow oxidation yields a yellow powder. The black material had infrared bands at:

2940 - 2860 (m)	cp? (a little low)
1995 s, 1985 s, 1940 s	co
1180 - 1000 (m) broad	cp
825 m, 634 m, 575 s	cp

Approximately the same spectrum was obtained from $cpFe(CO)_2SnCl_3$ LAH .

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SYNTHESIS OF LINEAR TRIMETALLIC MONOMERS

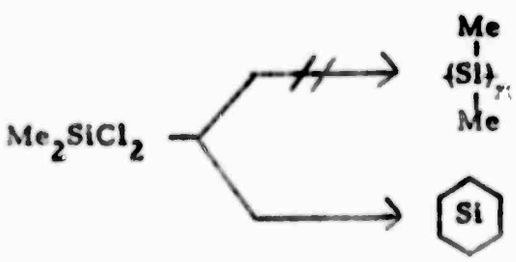
Don Murphy

It is now recognized that metal-metal bonds are generally stable. Nearly all possible combinations of metal-metal bonds have been synthesized. However, there are no high molecular weight polymers (one dimensional) with a backbone of metal-metal bonds, analogous to carbon systems. The closest systems to date are a variety of square planar d^8 metal complexes which crystallize with the metals "stacked" along one axis (1). X-ray data indicates there is no bond between the metals (metal-metal distances are typically 0.3 to 0.4 Å longer than the expected covalent distances, and for the most part they are monomers in solution), but there is an interaction as evidenced by anisotropic semiconductivity along the metal axis of 10^{-5} to 10^{-10} ohm^{-1} at room temperature. Some of the "stacked" complexes may be partially oxidized by halogens to give nonstoichiometric compounds which retain the stacked structure with the metal-metal distance reduced by about 0.2 Å. The conductivity in these systems is as high as 10^{-2} ohm^{-1} (2). Stacked crystals under high pressures (known to decrease the intermetallic spacing) improves the conductivity by as much as five orders of magnitude (3). It is felt that a polymer with actual bonds between metals would exhibit greater conductivity than the crystals, which have just an interaction.

The problems associated with the synthesis of linear high molecular weight polymers using metallic systems are numerous. The largest obstacle at the moment is a basic lack of knowledge of the chemical reactions of metals, in particular metal-metal bond forming reactions. The most commonly used reaction for making metal-metal bonds is the reaction of a metal anion with a metal halide

$$L_nM^{\ominus}\,Na^{\oplus} + \quad L'\,m\,M'X \longrightarrow Ln\,M\text{-}M'\,L'm + NaX,$$

which is only slightly more subtle than a Wurtz reaction. There are still enough reactions that it should be possible to form polymers if it is possible to eliminate unwanted polymerization. Nyholm (4) has shown that a system can often achieve lower energy by disproportionation to a form containing more metal-metal bonds. In particular, organometallic systems tend to cluster or cyclize when a one pot reaction designed to give a polymer is attempted.



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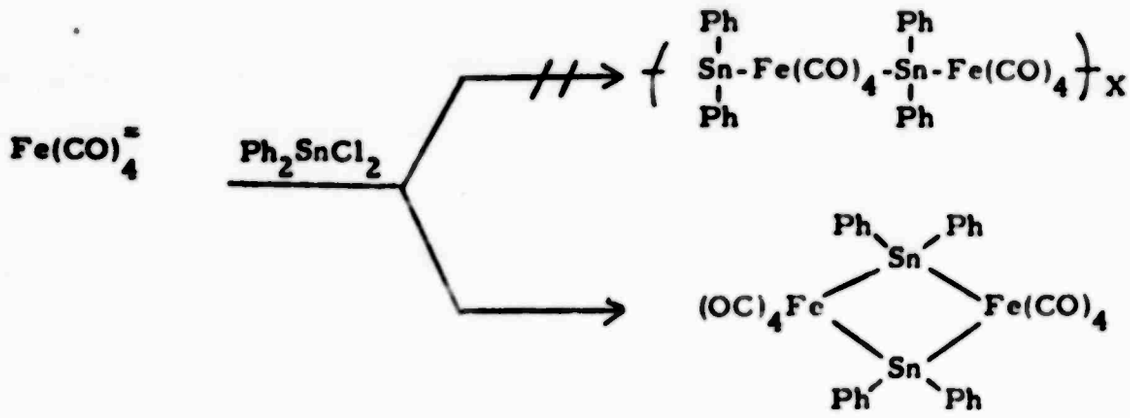


(6)

The approach to the problem then is to design systems in which cyclization or clustering cannot occur. Group IV metals are advantageous in that fairly large simple pieces are known, and tin has the only good coupling reactions to date (7).

$$-\overset{|}{\underset{|}{Sn}}-H + -\overset{|}{\underset{|}{Sn}}-H \xrightarrow{:B} -\overset{|}{\underset{|}{Sn}}-\overset{|}{\underset{|}{Sn}}- + -H_2$$

$$-\overset{|}{\underset{|}{Sn}}-H + R_2N-\overset{|}{\underset{|}{Sn}}- \longrightarrow -\overset{|}{\underset{|}{Sn}}-\overset{|}{\underset{|}{Sn}}- + HNR_2$$

Using group IV metals, there are two possible approaches: (A) classical wet methods involving a blocking group sequence and (B) reactions run on a polymer support to prevent cyclization. These have been discussed in reports by N. Nelson and R. Grubbs, and I will include only an experimental section containing the more important silicon compounds.

A transition metal system has the advantage of being truly linear if polymerization occurs in trans positions. Often when two metals are bound to a third they will occupy cis positions or be able to isomerize to the cis form fairly easily. Metal-metal bonds are generally "soft", thus the more stable isomer is expected to have metallo ligands trans to back-bonding ligands, which then leaves two metallo ligands cis to each other.

$$Ru(CO)_4 \xrightarrow{R_3SnCl} (R_3Sn)_2\ Ru(CO)_4 \qquad (8)$$

R = Me, Et, Pr, n-Bu, Ph

% cis 100 $\xrightarrow[\text{trans increases}]{\text{mix cis trans}}$ 0

$$Fe(CO)_4 \xrightarrow{R_3SnCl} (R_3Sn)_2\ Fe(CO)_4 \qquad (9)$$

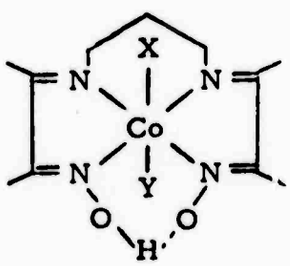
R = Me, Et, n-Bu, Ph

all cis

The $(R_3Sn)_2$-$Fe(CO)_4$ and $(R_3Sn)_2Ru(CO)_4$ series illustrate the relative strengths of steric and electronic effects on configuration. The Ru series goes from pure cis to pure trans as R becomes more bulky, while the Fe compounds are all cis. Steric effects should be larger with the smaller Fe

center. Electronically, the Ru center is somewhat "softer", allowing more back donation to the CO groups than the "harder" Fe center. This implies that it may be possible to make a linear system with a third row transition element, but not with a first row element.

A hopeful method for preventing a cis configuration is the employment of a tetradentate ligand constrained to occupy four coplanar positions. One such system which has been worked on by Costa (10) is cobalt complex of bis (diacetylmonoxime-imino) propane 1, 3, $((DOH)_{2pn})$.



$= Co(DO)(DOH)_{pn}XY$

X = Y = I, Br, Cl, CH_3, $Ph\text{-}CH_2$, Ph

It is generally possible to make other group IV derivatives when analogous carbon compounds are known (though not necessarily with the same ease!) This generalization along with the good coupling reaction for tin led to the general scheme

$$Co(DO)(DOH)_{pn}I_2 \longrightarrow Co(DO)(DOH)_{pn}(SnR_2Cl)_2$$

$$(R_2SnCo(DO)(DOH)_{pn}SnR_2)_X \longleftarrow Co(DO)(DOH)_{pn}(SnR_2H)_2$$

Cobalt carbon bond forming reactions and their tin counterparts are outlined below:

			Yield
$Co(DO)(DOH)_{pn}I_2$	$\xrightarrow{XsRMgX}$	$Co(DO)(DOH)_{pn}R_2$ R = Me, Ph, Ph-CH_2	Good
	$\xrightarrow{1\ mole\ RMgX}$	$Co(DO)(DOH)_{pn}RI$	Good
	$\xrightarrow{Ph_3SnLi}$	$Co(DO)(DOH)_{pn}(SnPh_3)_2$	10%
	$\xrightarrow[RX,\ EtOH]{NaBH_4}$	$Co(DO)(DOH)_{pn}RI$ + $Co(DO)(DOH)_{pn}R2$	Good
	$\xrightarrow[XsPh_3SnCl,\ EtOH]{XsNaBH_4}$	$Co(DO)(DOH)_{pn}(SnPh_3)_2$	25%
	$\xrightarrow[XsPh_3SnCl,\ EtOH]{<1mole\ NaBH_4}$	$Co(DO)(DOH)_{pn}(SnPh_3)I$	50%
	$\xrightarrow[2.\ Ph_3SnCl]{1.\ Na(Hg),\ THF}$	$Co(DO)(DOH)_{pn}(SnPh_3)_2$	10%
$RCo(DO)(DOH)_{pn}I$	$\xrightarrow[2.\ R'X]{1.\ Na(Hg)THF}$	$Co(DO)(DOH)_{pn}RR'$	Good

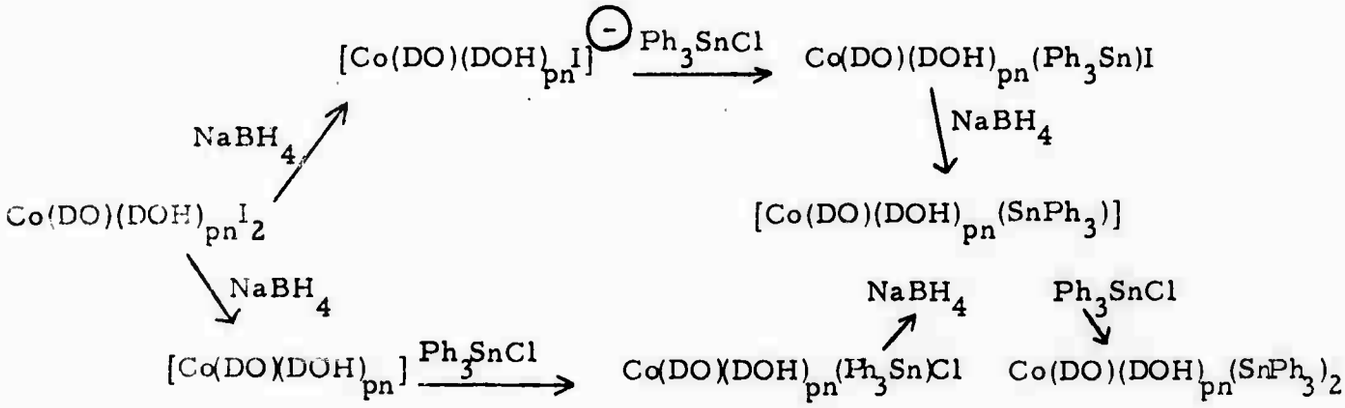
		Yield
$\xrightarrow[R'X,\ EtOH]{NaBH_4}$	$Co(DO)(DOH)_{pn}RR'$	Good
$\xrightarrow[2.\ Ph_3SnCl]{1.\ Na(Hg),\ THF}$	$Co(DO)(DOH)_{pn}R(SnPh_3)$	

The reduced cobalt species are oxidized rapidly by ethanol, so reactions in this solvent must be done in situ. Reactions in THF are done stepwise, since the reduced species is stable.

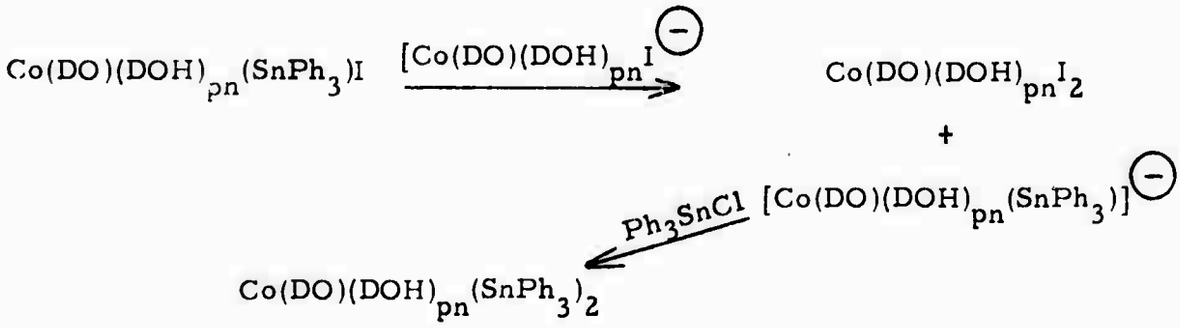
There is evidence that the reduced Co(I) species may exist in two forms, $Co(DO)(DOH)_{pn}I^-$ and $Co(DO)(DOH)_{pn}$. Evidence for the first form is derived from the initial formation of I $Co(DO)(DOH)_{pn}(SnPh_3)$ from the reaction of Ph_3SnCl and $Co(DO)(DOH)_{pn}I_2$ with $NaBH_4$ in ethanol, and the analogous reaction forming $Co(DO)(DOH)_{pn}RI$. Evidence for the second, neutral form comes from the reduction of $Co(DO)(DOH)_{pn}I_2$ in ethanol with $NaBH_4$. A blue solution initially forms which rapidly turns brown as ethanol oxidizes the Co(I). In the presence of Ph_3P, however, the Co(I) is stabilized and an air sensitive blue solid identified as $Co(DO)(DOH)_{pn}PPh_3$ by Costa precipitates. Costa found that this complex undergoes oxidative reactions.

$$Co(DO)(DOH)_{pn}PPh_3 \xrightarrow[PhH,\ reflux]{Ph{=}CH_2I} [Ph\text{-}CH_2\text{-}Co(DO)(DOH)_{pn}PPh_3]I$$

The complex fails to react with Ph_3SnCl after two days refluxing in benzene. A possible explanation for bis organo and organotin products from reduced Co(I) species is prior formation of a Co(III) halo organo species, followed by reduction by Xs Na BH_4. This may be illustrated for either proposed Co(I) species.



This scheme does not work for the THF reactions since there is no more reducing agent (Na(Hg)) when the tin is added. It is somewhat important that the nature of the reduced species and reaction mechanism in THF be elucidated so that yields of the bis products may be improved by altering conditions. It may be that Xs Co(I) reduces the initial product in a scheme such as:



In this scheme the Co(I) species must be an anion or be an equilibrium between neutral and anionic forms.

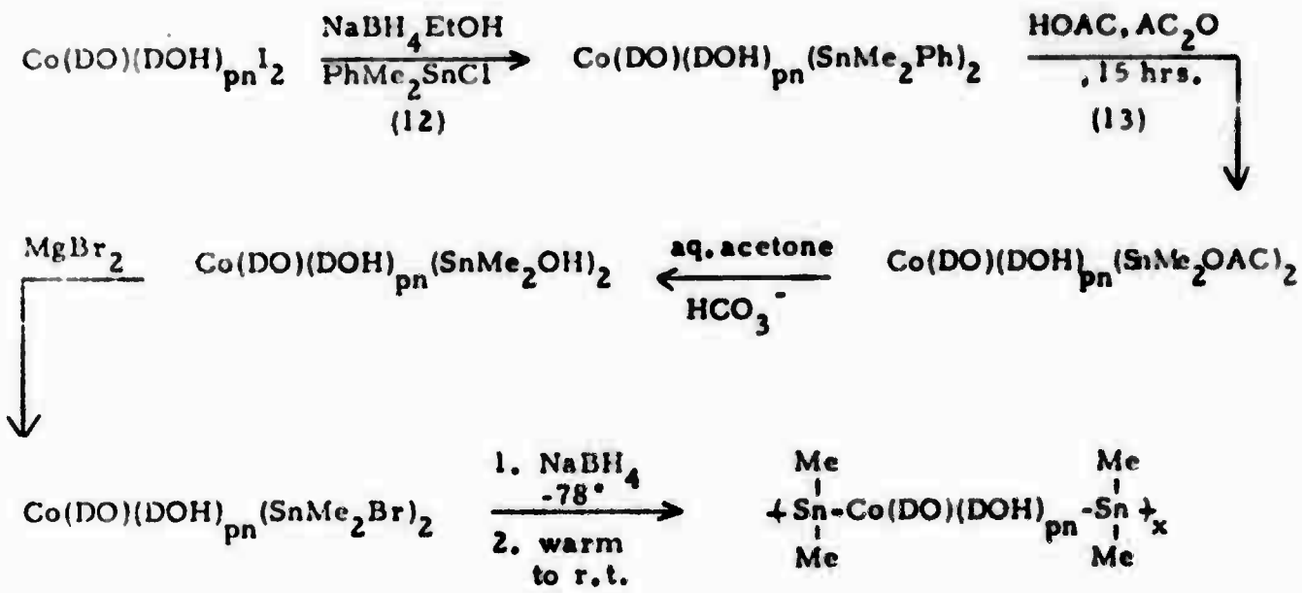
Of the cobalt tin bond forming reactions now at hand, only the stepwise reduction in THF followed by addition of Ph_3SnCl appears to be applicable to dihalo tin compounds to give bis (diorganohalo tin) cobalt complexes. Tlc of the reaction mixture of Ph_2SnCl_2 with Co(I) in THF show a small amount of $Co(DO)(DOH)_{pn}I_2$ and two new products (hopefully $Co(DO)(DOH)_{pn}(ClPh_2Sn)I$ and $Co(DO)(DOH)_{pn}(SnPh_2Cl)_2$,) but isolation of the pure products has not been achieved. To modify the borohydride prep to give halo tin products, a reducing agent that will reduce the $Co(DO)(DOH)_{pn}I_2$ but not the Sn-Cl bond is needed. BH_3 was chosen for this since it does not ordinarily reduce Sn-Cl bonds. From the reaction products, it appears that the reaction will not go to completion to give the bis complex,

$$Co(DO)(DOH)_{pn}I_2 \xrightarrow[Ph_2SnCl_6]{BH_3, EtOH} \begin{matrix} Co(DO)(DOH)_{pn}(Ph_2ClSn)I \\ \text{minor product} \\ + \\ I\text{-}Co(DO)(DOH)_{pn}\text{-}SnPh_2\text{-}SnPh_2\text{-}Co(DO)(DOH)_{pn}I \\ \text{major product} \end{matrix}$$

Failure to give bis complexes may be due to precipitation of products from solution and preferential reaction of BH_3 with ethanol, rather than the mono tin product. Use of THF rather than ethanol in an attempt to eliminate these problems gave a product containing I, Cl, and Sn, but no phenyl groups.

Attempts are continuing to isolate $Co(DO)(DOH)_{pn}(SnPh_2Cl)_2$. The reduction to the hydride and polymerization should be relatively easy, judging from the BH_3 reaction mentioned previously, and the stability of $(Ph_3Sn)_2Co(DO)(DOH)_{pn}$ to $NaBH_4$ (one prep used Xs $NaBH_4$). The halo tin cobalt complexes should be more stable than the organo tin complexes, as found by Schrauzer (11) with $Co(DMG)_2B$ derivatives.

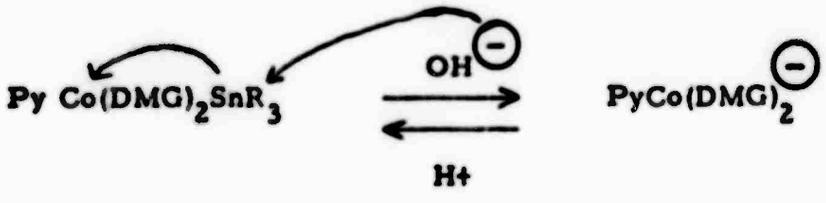
An alternative approach, which appears possible, involves preparation of an unsymmetrical bis trioganotin complex, selective cleavage of one of the organo groups, conversion to the halide, then reduction and polymerization.



To date, no alkyl tin complexes have been made with this system, after relatively few attempts. Schrauzer reports they are somewhat less stable in the DMG series (11). The HOAC cleavage of Sn-Ph bonds was demonstrated by Wiberg (13).

$$Ph_3Sn\text{-}SnPh_3 \xrightarrow[AC_2O,\ \ 15\ hrs.]{HOAC} (OAC)_3Sn\text{-}Sn(OAC)_3$$

Both $Co(DO)(DOH)_{pn}(SnPh_3)_2$ and $Co(DO)(DOH)_{pn}(Ph_3Sn)I$ appear to be able to withstand these conditions, i.e. after 15 hours reflux, both solutions retained their color, the bis complex light orange and the mono red. Benzene was detected in the vpc from both reactions, the amount was small, possible because after 15 hours at 115°C, benzene could have been lost through the reflux condensor (only 5 to 10 mg. was expected). The acetate hydrolysis is very mild. The compounds should be somewhat base sensitive (Schrauzer (11) found:



concentrations not specified), but there should be no problem. The $MgBr_2$ halogenation has been performed on Et_3SnOH in ether with a stoichiometric amount in 86% yield.

Experimental Section

dodecamethylcyclohexasilane (15)

The reaction was run in a 3 l round bottom flask fitted with a mechanical stirrer, condensor, and an addition funnel, under nitrogen. Me_2SiCl_2 (223g = 1.73 moles) was added over 1-1/2 hours to 1 l of refluxing THF, freshly distilled from LAH, containing 28.5g sodium (1.24 moles), 110g potassium (2.82 moles) and 3.4g naphthalene. The solution was refluxed for 30 hours, then hydrolyzed with ethanol, filtered, dried over Na_2SO_4, and retovaced to dryness. The crude product was extracted with 60 - 68° pet ether, filtered through silica gel, and crystallized from pet ether-acetone. Yield 60 - 80%.
M. W. in benzene: found 355; expected = 348.

1,6 dichlorododecamethylhexasilane (16)

$(SiMe_2)_6$ (44g), PCl_5(34g) and tetrachloroethane (200 ml freshly distilled) were mixed in a 2 l round bottom fitted with a long condenser under nitrogen. The mixture was then allowed to contact a preheated (165°) oil bath. After about a three minute induction period, the reaction became quite exothermic (the reason for the over-sized flask), the oil bath was quickly removed, until the mixture was just boiling, the heat was then applied for 12 additional minutes. The solvent was stripped

under vacuum at 20 - 40°. After refrigeration, crystals of $(SiMe_2)_6$ precipitate. Distillation of the mother liquor at 0.1 mm gave a liquid forerun up to 80°, $(SiMe_2)_6$ 100 - 110°, and Cl-$(SiMe_2)_6$ - Cl at 135 - 140° C. Twice distilled product was pure by vpc. The product is a white solid at room temperature. Yield = 18g = 40%.

1-phenyl-6-chlorododecamethylhexasilane

Slow addition of 0.75 ml of 2.14 M PhLi (1.60 mmoles) to 0.40g Cl-$(SiMe_2)$ - Cl (1.14 mmoles) in 5 ml ether at -78°C under nitrogen gave a mixture of the dichloro, diphenyl, and phenylchloro derivatives. The desired product was isolated by preparative glc at 210°C using a 6 ft., 1/2 in., 10% SE 30 column, with a flow rate of 150 cc/min. and 0.8 ml injections. Yield 68 mg (15%). Attempts to scale up the reaction and separate the products by vacuum distillation failed due to thermal isomerization. Nmr shows six distinct types of methyl protons. The integration Ph/Me = 7.3, expected = 7.2.

1,6 triphenyltindodecomethylhexasilane

Lithium triphenyltin (1.8 mmoles), made by stirring Ph_3SnCl (600 mg) with excess lithium in THF under argon, was slowly added to a THF solution of Cl$(SiMe_2)_6$ - Cl (300 mg = .85 mmoles) at 0°C. After two hours the solution was filtered, then stripped to give a white product. Recrystallization from hexane gave a pure product by tlc (R_f = .8 on Si gel with 3:1 CH_2Cl_2 - Et_2O). Integral ratio Ph/Me = 0.82, exptected = 0.83.

bis (diacetylmonoxime-imino) propane 1, 3 (17)

$(DOH)_2pn$

A diisopropyl ether solution (500 ml) of butanedionemonoxime (90g = 0.90 moles) and 1, 3 propanediammine (36g = 0.45 moles) was slowly heated to first boiling (ca. 30 min.), then slowly cooled to room temperature with stirring. The mixture was placed in the refrigerator overnight to crystallize, filtered, and washed with ether. Yield = 95g = 80%. Used in subsequent reactions without recrystallization.

1(diacetylmonoximato-imino) - 3 - (diacetylmonoxime-imino) propane cobalt diiodie (10a)

To an ethanolic solution of $(DOH)_{2pn}$ (90g in 900 ml) an aqueous solution of $CoCl_2 \cdot 6H_2O$ (90g in 600 ml) and KI (100 ml saturated solution) was added. Oxygen was bubbled through the solution for two hours, during which dark green crystals precipitated. The mixture was filtered, washed with water, ethanol, and ether. The product was recrystallized from acetone-ethanol. Yield = 33g = 16%.

bis(triphenyltin)1-(diacetylmonoximato-imino)-3-(diacetylmonoximeimino) propane cobalt

Method A:

$$Co(DO)(DOH)_{pn}I_2 \xrightarrow[NaBH_4, EtOH]{Ph_3SnCl} (Ph_3Sn)_2Co(DO)(DOH)_{pn}$$

To a stirred solution of Ph_3SnCl (200 mg = 0.53 mmoles) and $Co(DO)(DOH)_{pn}I_2$ (100 mg = 0.18) in 50 ml ethanol, 200 mg $NaBH_4$ was slowly added through a tipping tube. An orange precipitate resulted which was filtered, dissolved in CH_2Cl_2 and filtered through a three inch column of silica gel washed with deoxygenated CH_2Cl_2. The product was then crystallized with ethanol to give orange, air stable crystals. Yield = 60 mg = 30%.

Method B:

$$Co(DO)(DOH)_{pn}I_2 \xrightarrow[THF]{Ph_3SnLi} (Ph_3Sn)_2Co(DO)(DOH)_{pn}$$

Lithium triphenyltin (0.42 mmoles), prepared by stirring excess Li (2.0g) with hexaphenylditin (150 mg = 0.21 mmoles) in THF under argon for four hours, was slowly added to a solution of $Co(DO)(DOH)_{pn}I_2$ (150 mg = 0.27 mmoles) in 25 ml THF under nitrogen. After fifteen minutes the mixture was concentrated, addition of ether precipitated an orange product. The product was recrystallized from THF: hexane. Yield = 35 mg = 15%. Product identical with Method A by i. r. and tlc.

Method C:

$$Co(DO)(DOH)_{pn}I_2 \xrightarrow[2.\ Ph_3SnCl]{1.\ Na(Hg),\ THF} (Ph_3Sn)_2Co(DO)(DOH)_{pn}$$

A THF solution (20 ml) of $Co(DO)(DOH)_{pn}I_2$ (50 mg = 0.09 mmoles) was stirred with an excess of Na(Hg) for four hours under nitrogen. The blue solution was filtered in an inert atmosphere. To the filtered solution, 100 mg Ph_3SnCl (0.27 mmoles) in 20 ml THF was slowly added. The product was isolated as in Method A. Yield = 10 mg = 10%. Product identical with that from Method A.

<u>triphenyltin 1-(diacetylmonoximato-imino)-3-(diacetylmono ime-imino) propane cobalt iodide</u>

Modifying Method A for $(Ph_3Sn)_2Co(DO)(DOH)_{pn}$ by essentially titrating to the disappearance of $Co(DO)(DOH)_{pn}I_2$, the mono substituted derivative is obtained. To 1.0 g $Co(DO)(DOH)_{pn}I_2$ and 2.0g Ph_3SnCl in 400 ml degassed ethanol, $NaBH_4$ was added a few crystals at a time through a tipping tube. The solution turned magenta, and orange brown crystals appear along with the green starting material. Every few minutes, more $NaBH_4$ was added until all the starting material was gone. The solution was stirred an additional hour, filtered, washed with ethanol and ether. Crude yield = 0.84g = 60%. An attempt to recrystallize from CH_2Cl_2 - EtOH gave $Co(DO)(DOH)_{pn}I_2$. A portion was successfully filtered through a column of degassed silica gel with CH_2Cl_2 and crystallized from CH_2Cl_2 - Et_2O.

$I(DO)(DOH)_{pn}Co(SnPh_2)_2Co(DO)(DOH)_{pn}I$

To a solution of Ph_2SnCl_2 (5.0g) and $Co(DO)(DOH)_{pn}I_2$ (3.0g) in 250 ml ethanol at -78°C was added 30 ml 3M BH_3 (THF solution) and stirred for two hours, then warmed to 0°C for two more hours. An orange precipitate resulted, filtered, washed, with ethanol and ether, and recrystallized from acetone. Yield = 1.4g = 20%. A portion was filtered through a degassed silica gel column with CH_2Cl_2. The reaction sometimes gives a product containing Cl, probably a mixture of $I\text{-}Co(DO)(DOH)_{pn}(SnPh_2Cl)$ and $I(DO)(DOH)_{pn}Co(SnPh_2)_2Co(DO)(DOH)_{pn}I$. Molecular weight in THF: found = 1397, expected = 1396.

nmr of silicon compounds vs. TMS in ppm(δ)

$(SiMe_2)_6$	0.16(s)					
$Cl\text{-}(SiMe_2)_6\text{-}Cl$	0.58(s)	0.32(s)	0.30(s)			
$Ph\text{-}(SiMe_2)_6Cl$	0.49(s)	0.40(s)	0.21(s)	0.19(s)	0.16(s)	0.01(s)
$Ph_3Sn(SiMe_2)_6SnPh_3$*	.050 (t) $J_{Sn\text{-}H}$ = 10 H.		0.10(s)		0.05(s)	

*Integral ratios of Ph protons to Me protons agrees with expected result.

ir of cobalt complexes in Cm^{-1}

$Co(DO)(DOH)_{pn}I_2$	1495(s)	1420(m)	1350(m)	1275(m)	235(m)
	1130(s)	1080(w)	995(w)	870(m)	830(w)
	870(m)	795(s)	600(bd)	435(m)	

Spectra of all phenyl tin derivatives look nearly identical to the $Co(DO)(DOH)_{pn}I_2$ spectra with a few extra peaks for Ph groups. The intensities of the Ph peaks correlate with the number of Ph groups.

Ph peaks	1420(s)	1000(s)	730(s)	450(s)

Elemental analysis of cobalt complexes

$Co(DO)(DOH)_{pn}(Ph_3Sn)_2$

	C	H	N
expected	56.53	4.95	5.61
found	56.25	4.99	5.65

$(ICo(DO)(DOH)_{pn}Ph_2Sn)_2$

	C	H	N	Cl	I
expected	39.55	4.19	8.02	0.00	18.19
found	36.73	3.90	7.71	0.00	20.85

$Ph_3SnCo(DO)(DOH)_{pn}I$

	C	H	N	Cl	I
expected	44.91	4.43	7.23	16.38	0.00
found	44.86	4.45	7.34	15.37	0.00

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IV. X-RAY CRYSTALLOGRAPHIC STUDIES

The X-ray work involved in the studies of the Krogmann salts thus far has not been an elaborate one. The X-ray diffraction technique is used to determine the metal-metal distances in the crystals and their crystal habits, as well as providing the simplest and most sensitive method of identification for these compounds.

In the beginning, we were able to prepare only powder crystals of the oxidized compounds, from which Guinier photographs were made. These powder patterns were run both at Stanford's Center for Materials Research and in our X-ray laboratory. Fig. 1 is the spectrum of the parent compound, $K_2Pt(C_2O_4)_2 \cdot 2H_2O$, and Fig. 2 shows a spectrum of the oxidized salt, $K_{1.62}Pt(C_2O_4)_2 \cdot 2H_2O$. It can be seen that they have distinctly different spectra, their most striking difference being the d-spacings of the inner rings and their different intensities.

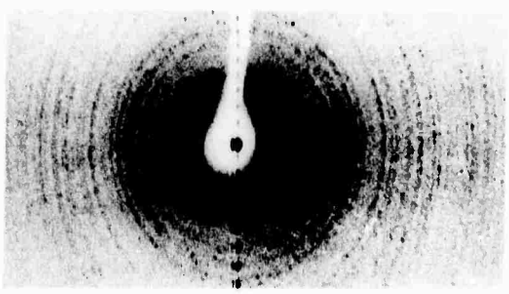


Fig. 1 Powder pattern of parent compound, $K_2Pt(C_2O_4)_2 \cdot 2H_2O$.

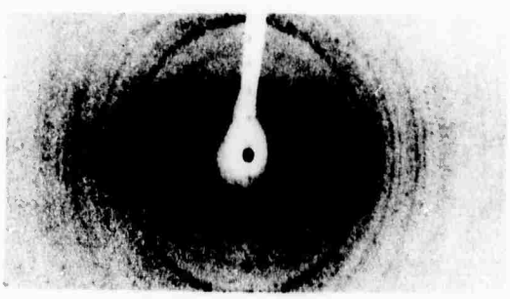


Fig. 2 Powder pattern of oxidized compound, $K_{1.62}Pt(C_2O_4)_2 \cdot 2H_2O$.

Single crystals of both the potassium and magnesium salts have later been obtained by repeated recrystallization from water. Photographic X-ray data were taken on one of these crystals usually with the dimensions 0.2mm. x 0.05mm. x 0.5mm. The oscillation and zero-level Weissenberg photographs revealed that the crystal of the potassium oxidized salt was triclinic (i.e. no crystallographic symmetry, all axes of unequal length, and all interaxial angles unequal and not equal to 90 degrees); whereas those of the corresponding magnesium salt belong to a hexagonal space group (characterized by 2 axes 120 degrees apart, which are equal in length, these 2 axes are both perpendicular to the third axis which is not of the same length).

One advantage we have in these Krogmann compounds is that the Pt atoms are far stronger scatterers of x-rays than the other atoms (by a factor roughly equal to the ratio of their atomic numbers, 78/6), thus giving intense layer-lines on the photographs, (see Figs. 3 and 4), which enabled us to determine the Pt-Pt distances easily. From simple calculation based on the distances between these intense layer-lines, the Pt-Pt distances were found to be 2.85 and 2.87Å for the potassium and magnesium oxidized salts respectively.

In taking these oscillation photographs, the crystals were mounted either on thin glass fibers or in thin-walled capillaries, at the center of a piece of film mounted in a cylindrical holder, which is slotted to permit the entry of x-ray beams. Radiation of Cu K-α rays with a Ni filter was used, and the exposure times were about two hours.

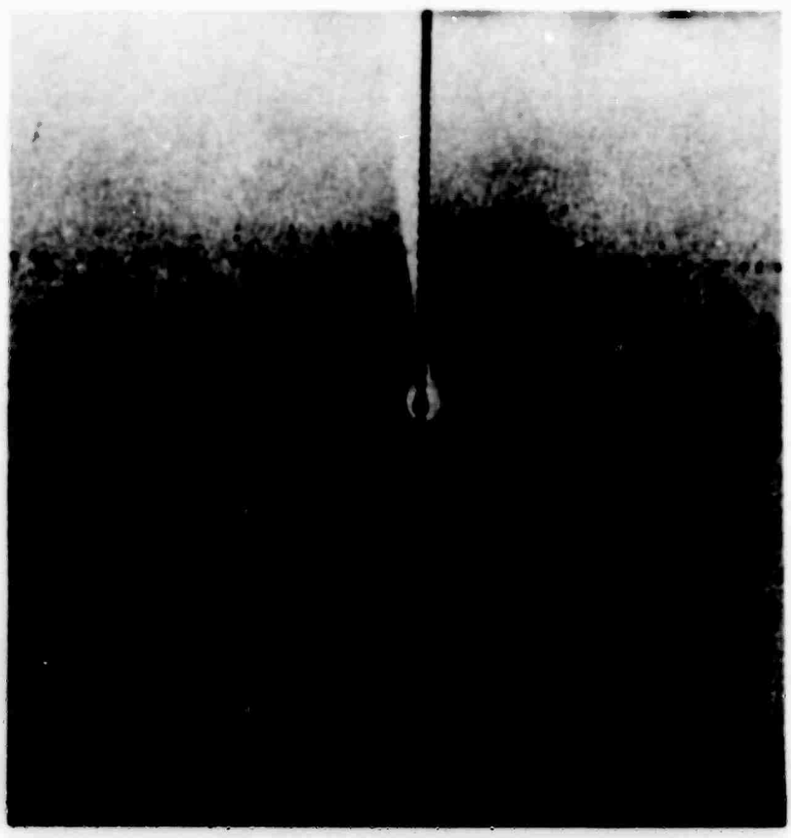


Fig. 3 Oscillation photograph of $K_{1.62}Pt(C_2O_4)_2 \cdot 2H_2O$.

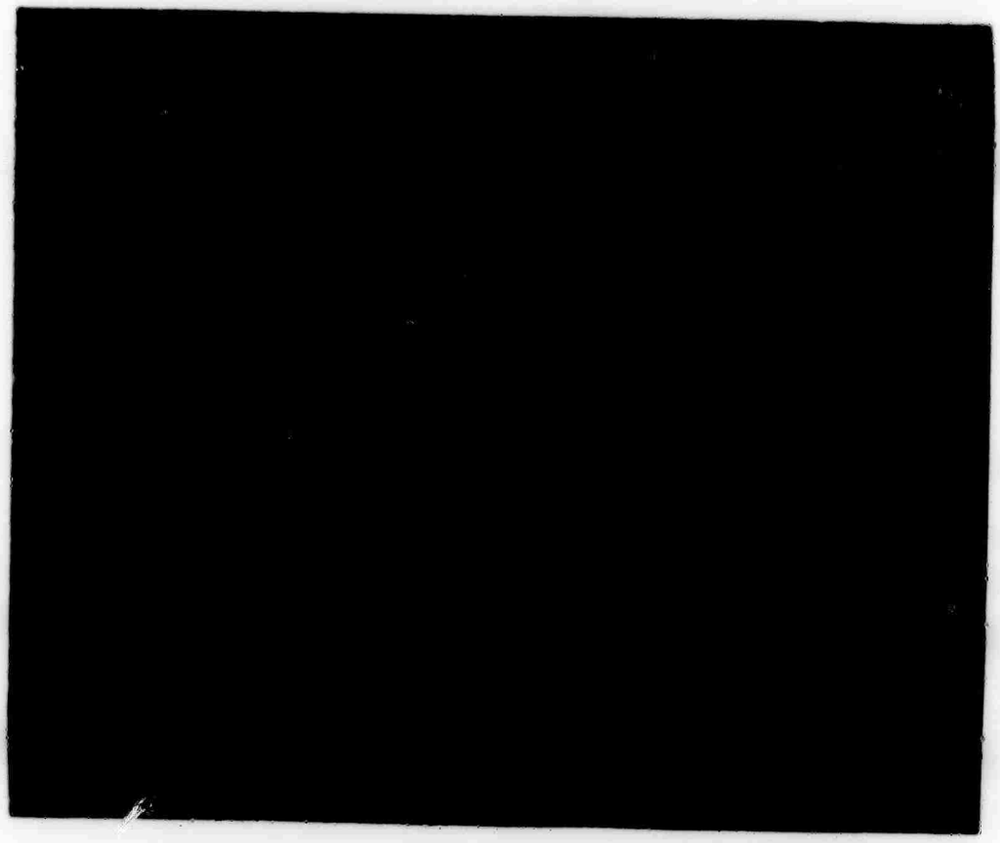


Fig. 4 Zero-level Weissenberg photograph of $K_{1.62}Pt(C_2O_4)_2 \cdot 2H_2O$.

The X-ray work for studies of the Sn_2-Co compounds (see Synthesis section) is more difficult because the metal atoms do not dominate the scattering to the extent they do in the Pt-compounds. Data on the unit cell dimensions was first obtained and then 2,400 diffraction peaks measured from which a Patterson function was obtained. The three metal atoms were located. After a least-squares refinement of the position and determination of the anisotropic thermal motion parameters of these atoms was completed, an electron density map of the structure was prepared. From the map twelve of the seventeen atoms in the porphyrin ring and four of the phenyl groups attached to the two tins were tentatively located. This partial structure is being refined and from the refined electron density map the remaining atoms should be located.

V. EXPERIMENTAL PROGRAM: Physical Measurements

A. Introduction

The materials to be studied are generally in the form of brittle needle-shaped crystals of the order of a millimeter in length and a tenth of a millimeter diameter. These have been studied under an optical microscope (Fig. 1) and in a scanning electron microscope (Fig. 2). Samples such as these are obviously difficult to manipulate for physical measurements; and so a program has been started to find the best conditions for growth of large single crystals.

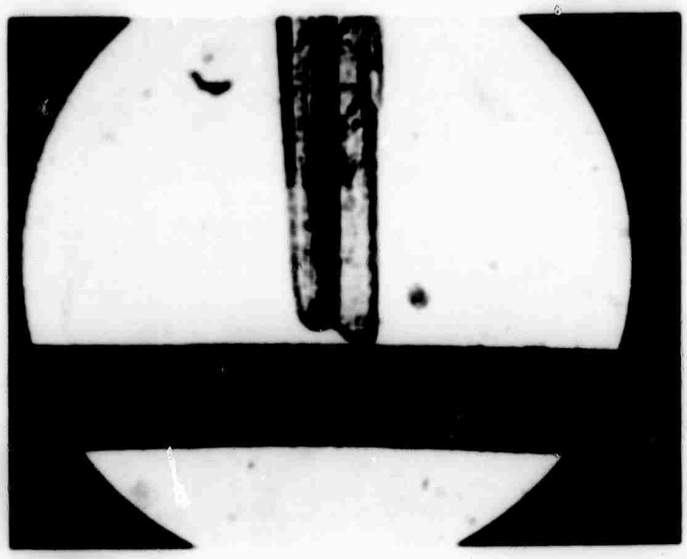
The physical properties of principal interest are the electrical conductivity under various conditions, and the excitation spectra of the solids. Conductivity measurements have been made on single crystals at room temperature, and on compressed pellets down to about 20K. Apparatus is being constructed to extend these to four-probe measurements on single crystals at all temperatures, conductivity under pressure to 10 kilobars, photoconductivity and conductivity perpendicular to the axis of the crystals. Finally, Raman spectra and the possibility of specific heat measurements are being investigated as a means of finding the Debye temperature and other basic properties.

B. Materials

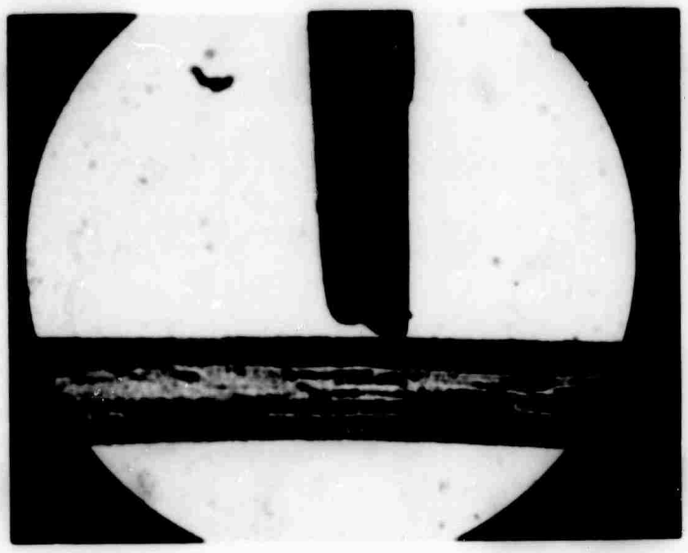
$K_{1.62}Pt(C_2O_4)_2 \cdot 2H_2O$: "Oxalato Complex"

$K_2[Pt(CN)_4]Br_{0.3} \cdot 2.3H_2O$: "Cyano Complex"

These have been the most extensively studied, and will be referred to by the names above.

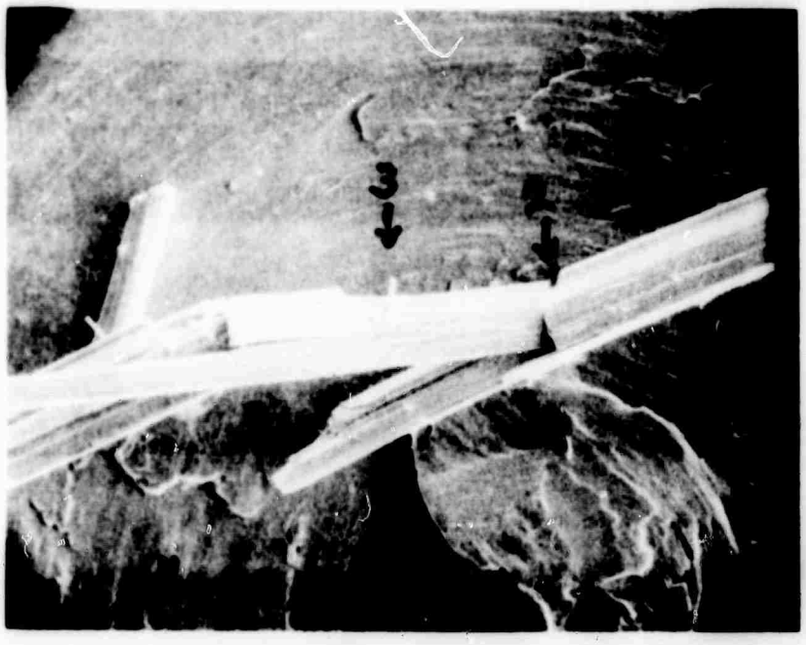


(a)

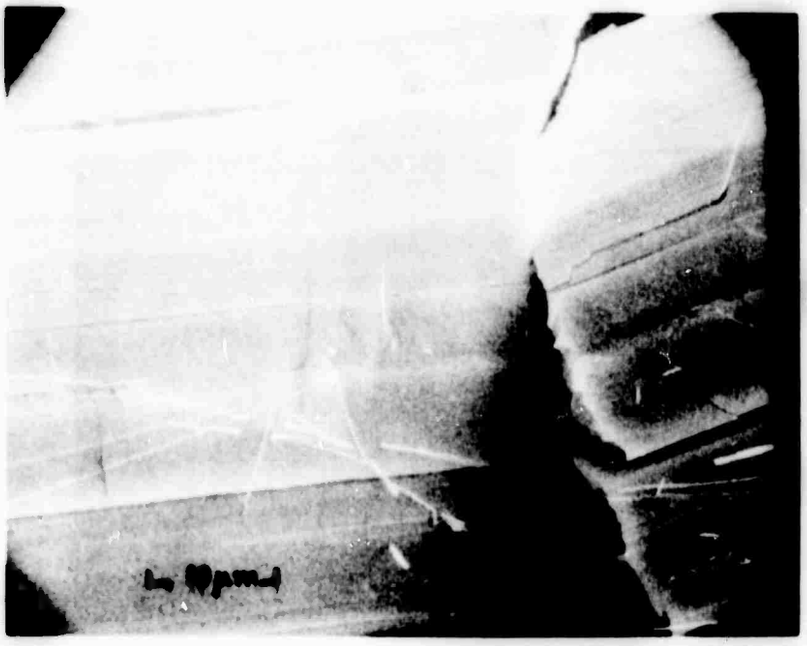


(b)

Fig. 1 Oxalato Complex under optical microscope 600×.
(a) Transmitted light, plane of polarization horizontal.
(b) Transmitted light, plane of polarization vertical.



(a)



(b)

Fig. 2 Scanning electron microscope picture of oxalato complex, showing fracture which occurred under vacuum.
(a) 180×.
(b) Fracture at "2" with magnification 1800×.

$[Sr - (Co)]_x$ prepared by Collman Group

Poly 9-vinyl Anthracene (from S.R.I.)

have been found essentially non-conducting, $\sigma < 10^{-10}$ ohm^{-1}cm^{-1}.

1,1 Diethyl-2,2 Cyanine TCNQ Complex

has been found non-ohmic but with effective conductivity falling as the temperature is reduced (effective $\Delta \sim 0.2$eV).

C. Crystal Growth

The Oxalato and Cyano complexes are both to be recrystallized from aqueous solution. When a few drops of hot, saturated oxalato complex solution were evaporated from a microscope slide, three distinct growth patterns were observed. A few large, fairly regular crystals were formed (Fig. 1); and most of the slide was covered with a fine tracery of ~ 1μm hair-like crystals. However, in certain regions parallel-sided crystals were formed, approximately 10μm on a side. The same growth patterns can be observed on the large crystals when observed in the scanning electron microscope (Fig. 2). An investigation is under way to find the conditions for growth in this regular form. A set of solutions is being evaporated at temperatures every few degrees between 80 and 20°C. From these the solubility and crystal form of each will be determined. When the optimum is found, then it will be applied to growth in an incubator with a very slowly varying temperature (~1° per day). Other factors in growth, such as acidity of the solution, will also be studied.

D. Electrical Conductivity

All of the measurements so far made are somewhat uncertain because of surface or contact effects. For instance, the apparent conductivity of a compressed pellet of the cyano complex could be increased several orders of

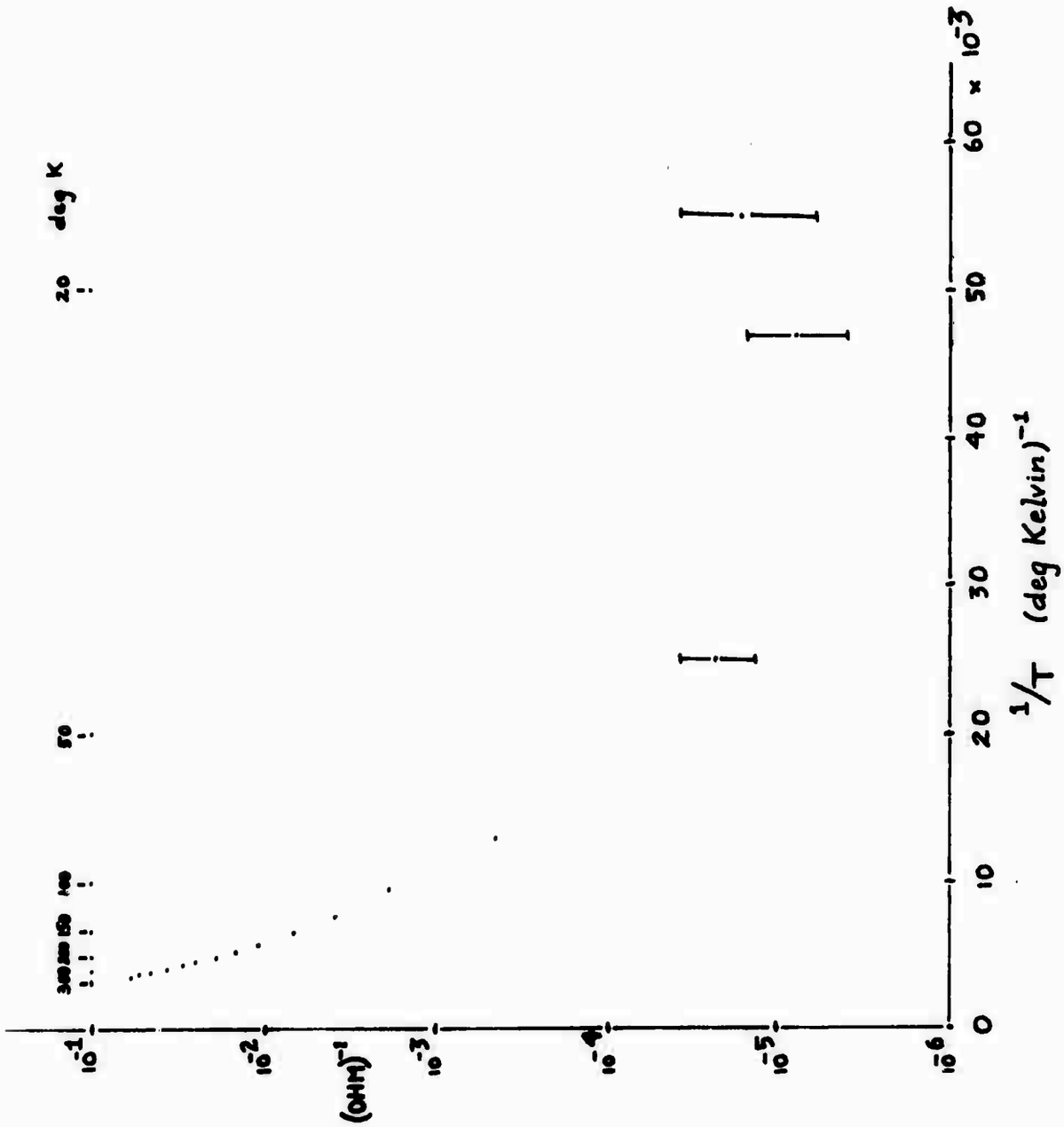


Fig. 3 Log conductance of pellet of oxalato complex plotted against inverse temperature (measurements at 10V).

magnitude by breathing on it, presumably due to moisture affecting the surface. Under constant, low humidity this same pellet showed a conductivity increasing with increasing voltage, but becoming irreproducible above a few volts.

Measurements on the Oxalato complex have shown similar problems, and more detailed investigation is in progress. However, two measurements are of interest:

1. On a single crystal at room temperature the conductivity was found to be fairly reproducible at $\sigma \approx 1.5\ 10^{-3}$ ohm^{-1}cm^{-1}.

2. A compressed pellet of the substance showed only slight variation of conductivity ($\sigma \sim 10^{-4}$ ohm^{-1}cm^{-1}) with voltage between 2 and 10 volts. Therefore measurements were taken at one voltage as a function of temperature. Near room temperature the conductivity fell rapidly as the temperature was lowered but it became roughly constant near 20K. (Fig. 3) The variation was not a simple exponential with inverse temperature; but if assumed to be, at higher temperatures the slope corresponded to $\Delta \sim 0.03 - 0.05$eV.

E. Handling and Mounting the Samples

A micro-manipulator and stereo microscope is being used in attempts to attach the four electrical leads for current and voltage measurement. The brittleness of the crystals makes a strain free support necessary (see Fig. 2 where a crystal has sheared while under vacuum, perhaps due to loss of waters of crystallization). A frame has been constructed of anodized aluminum (insulating) over which fine gold wires are strung (Fig. 4). The crystal is then mounted across these wires and fixed with silver paint, which also gives electrical contact. This flexible support should be able to take up the contraction on cooling the crystals. However, in trials to date, the crystal has broken as soon as the refrigerator chamber is evacuated.

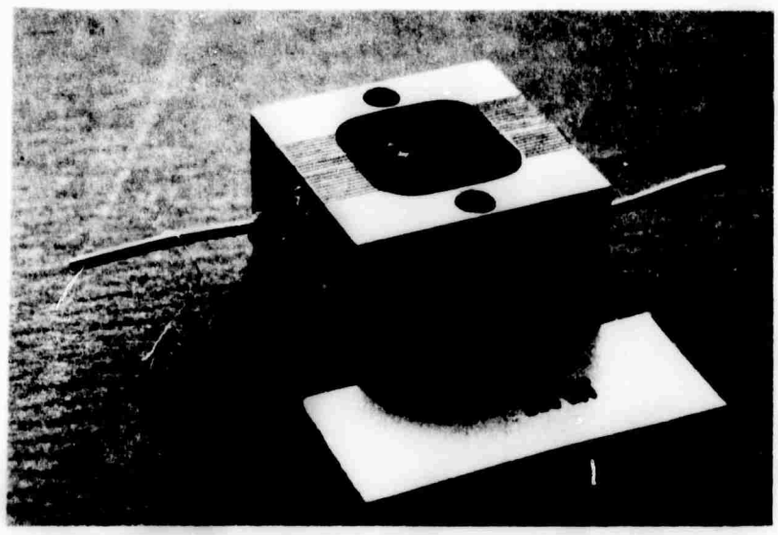


Fig. 4 Anodized aluminum frame for mounting crystal between flexible gold wires.